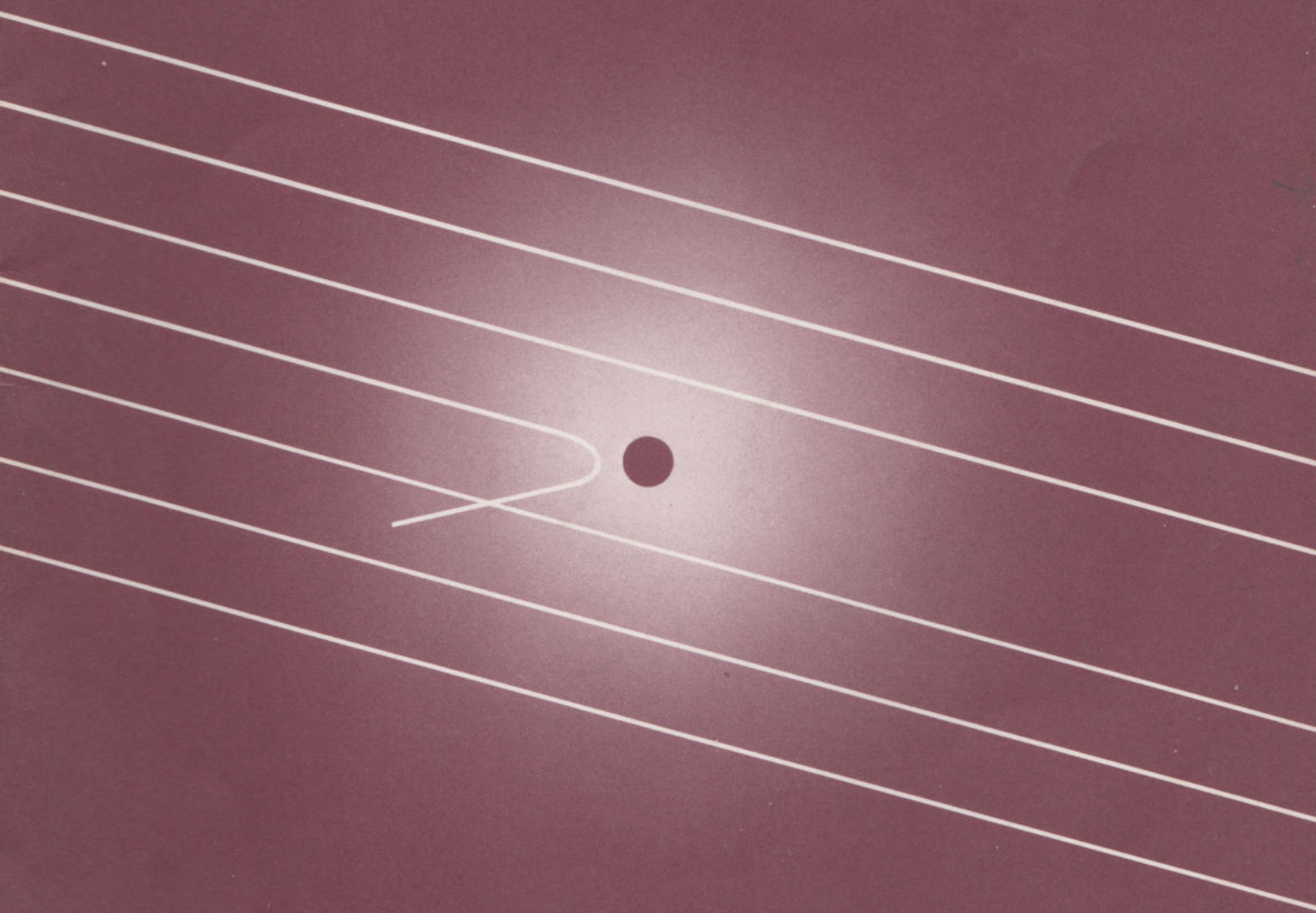
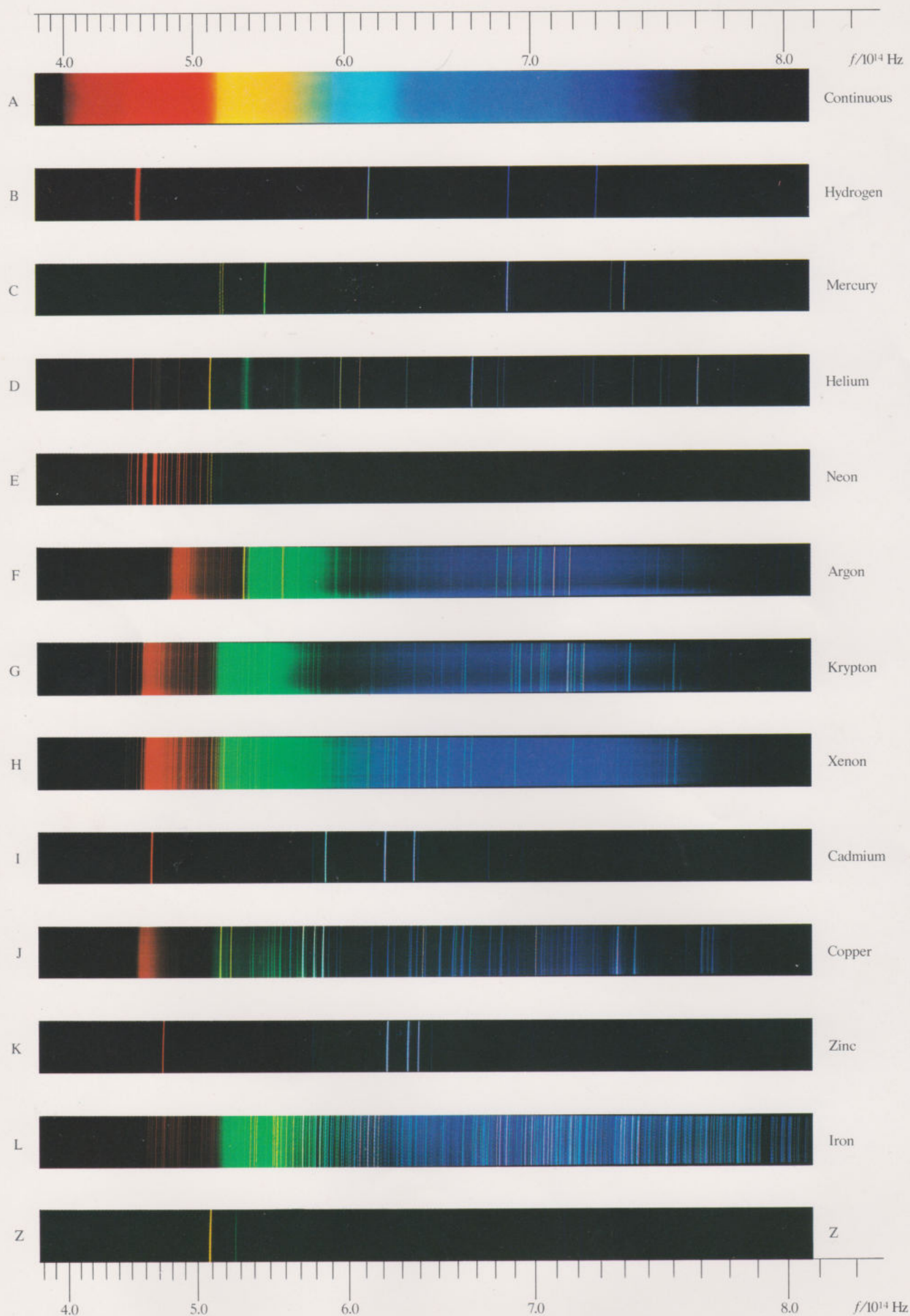




Atomic Structure





A continuous spectrum and the spectra of some elements. In the yellow/green region of these spectra the colours may not correspond exactly with those that you see in a spectroscope. This is due to difficulty in the photographic reproduction of this part of the spectrum. Some of the line spectra of the elements extend into the ultraviolet region; the continuous spectrum shown here is restricted to the visible region.



The Open University

Science: A Foundation Course

Units 10 and 11

Atomic structure

Prepared by the Science Foundation Course Team

The Open University Press

SCIENCE

S101 Course Team List

A note about the authorship of this text

This text is one of a series that constitutes a component part of the Science Foundation Course. The other components are a series of television and radio programmes, audio-vision materials, home experiments, assignments and a summer school.

The Course has been produced by a team that collectively accepts responsibility for it.

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Table A A list of terms and concepts used in Units 10 and 11

Assumed from general knowledge	Introduced in a previous Unit	Unit Section No.	Introduced in this Unit	Page No.
fluorescent screen in TV set microscope nuclear bomb nuclear power station	acceleration	3.2.2	absorption spectrum	30
	balance	4 (Home Experiment)	α -particles	19
			atom	22
	conservation of energy	8.3	atomic number, Z	22
	coulomb, C	8.10.2	atomic spectra	30
	Coulomb law	8.10.2	β -particles	25
	$E = hf$	9.6.2	balanced equation	12
	electrical force	8.10.2	carbon dating	27
	electron	9.6	chemical element	7
	electrostatic charge (+ and -)	8.10.2	continuous spectrum	29
	energy transfer	8.3.2	continuum	37
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	frequency, f	9.4.3	degeneracy	54
	gravitational energy	8.7	electric field	9
	uniform magnetic field	5.2.3	electric potential	13
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	interaction between moving electric charges	8.10.2	electron shell	42
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	mass	2.1.4	electronic configuration	48
	monochromatic radiation	9.6	electronic structure	29
	Planck's constant, h	9.6.2	emission spectrum	29
	photoelectric effect	9.6	energy-level diagram	34
	photon	9.6.2	excited state	36
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	velocity	3.2.1	Fraunhofer lines	30
	volt, V	8.10.3	γ -radiation	26
	X-rays	9.5.1	ground state	34
			half-life	26
			Hund's rule	58
			ion	12
			ionization energy, I	37
			isotope	16
			line spectra	30
			magnetic quantum number, m	55
			mass number, A	16
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			nuclear fission	27
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			nucleus	20
			orbital	21
			pairing of electrons	53
			photoelectron	43

Assumed from general knowledge	Introduced in a previous Unit	Unit Section No.	Introduced in this Unit	Page No.
			photoelectron spectroscopy	43
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Study Guide for Units 10 and 11

Units 10 and 11 cover one topic, the structure of atoms. Although there is a natural point where the Units could be divided (at the end of Section 4), you should aim to complete Section 5 by the end of your first week of study if you want to stay on schedule. There are two home experiments. One is in Section 2, and you should try to complete it before you finish Section 2; this one takes about 30 minutes. The other, in Section 5, involves only a few observations with the hand spectroscope; try to choose a bright day to observe the Sun's spectrum.

You will be able to follow TV 10 without having read any of the main text, although you may find some advantage in having read up to the end of Section 2 before viewing it. You should try to read through Section 5 before you watch TV 11, although this is not absolutely necessary to understand the programme. Radio 05 is broadcast during the first of the two study weeks for Units 10 and 11.

We have devised two ways to help you revise your knowledge of Units 10 and 11: the Units contain an audio-vision cassette (AC 757R, The Interpretation of Atomic Spectra), which should help your understanding of Sections 5 and 6; you will also be able to use a computer-assisted learning program (CALCHEM) by using the terminal at your Study Centre. This CALCHEM program gives you exercises on Sections 9 and 10, and revises some ideas in earlier Sections. Of course, a very useful way to revise any Unit, is to examine the summary at the end of each main Section. These contain the most important points and you should be certain that you understand them.

1 Elements and symbols

When you studied earlier Units of this Course, you will have noticed that we stated that all substances are composed of atoms, although we said rather little about atoms themselves. Perhaps you accepted this, or perhaps you wondered how scientists know about atoms. If so, you might have asked yourself questions of this sort: Can we see atoms? What do they look like? How big are they? Do they themselves have a structure? Are there many different kinds of atom and if so, how many?

In this double Unit we shall be examining the results of experiments that provide some answers to this kind of question. As you will see in later Units, this exploration of atomic structure is more than an exercise of man's curiosity about the world he lives in. An understanding of atomic structure is the first step towards an understanding of how different substances behave.

Let us start by examining the last of the questions suggested above. If all substances are composed of atoms, it seems logical to suppose that different substances are composed of different sorts of atom. Obviously, there is a vast number of different substances. So is there a vast number of different sorts of atom?

Your everyday experience tells you that some substances can be converted into others: petrol burns rapidly to produce gases which contain water vapour (you can see the water vapour condensing to liquid water on a cold day), and iron rusts slowly when exposed to the air.

To take the case of iron converting to rust, it seems plausible that one of these substances, iron or rust, contains the other combined in some way with another substance. If protected from the air by a layer of paint or chromium, iron does not rust. This seems to suggest that air is necessary for the formation of rust. In fact iron is the simpler substance which combines slowly with a component of the air, oxygen, to produce a different, more complex substance, rust. To take another example, you probably know that when you 'burn' vegetables while cooking, they form black carbon. Carbon too is a simple substance. It also seems plausible that every substance is composed of one or more simple substances of which there is perhaps a relatively small number.

Although this notion of simple substances occurred to ancient man, the scientific understanding of these simple substances has developed only over the past three hundred years. The ancient Greeks, who had a philosophical rather than a practical approach to problem-solving, thought that there were only four simple substances: air, earth, fire and water, which they called the elements. This idea did not stand the test of experiment, and we now know that there are many more than four. Although we still use the term *element* to describe a simple substance, none of the four Greek elements is in our present list. So how many elements are there?

About ninety elements occur naturally on the Earth, and scientists have managed to make nearly twenty others. Later in these Units you will discover how 'new' elements are made. However, we shall not follow the history of the recognition and discovery of the elements until Unit 12. The recognition that all substances are composed of a number of elements took place over centuries of careful experiment and logical interpretation. We shall start with the view held at the beginning of this century: that all substances are composed of one or more of the 90 naturally occurring elements.

With this number of elementary substances to deal with, the picture is already becoming complicated, especially if we want to describe substances that consist of several elements. To simplify matters, scientists have developed a shorthand notation for representing substances. Each element is represented by a *symbol*, often the first one or two letters of the name of the element*. Sometimes, particularly for elements that have been known for a long time, the symbol is derived from an old foreign (usually Latin) name. Some of the elements and their symbols are listed in Table 1, and a complete list is given in Appendix 1.

TABLE 1
Some elements and their symbols

Element	Symbol
aluminium	Al
argon	Ar
carbon	C
copper	Cu (from cuprum)
gold	Au (from aurum)
helium	He
hydrogen	H
iron	Fe (from ferrum)
lead	Pb (from plumbum)
magnesium	Mg
mercury	Hg (from hydrargyrum)
neon	Ne
nitrogen	N
oxygen	O
silicon	Si
silver	Ag (from argentum)
sodium	Na (from natrium)
sulphur	S
uranium	U
zinc	Zn

chemical element

symbols for chemical elements

* Note that when an element is represented by two letters, the first is a capital letter and the second a lower-case letter. Thus, aluminium is Al.

What does the symbol Au mean?

The symbol Au is our shorthand way of representing the substance gold. But a word of warning: these symbols can also be used to represent the smallest amount of an element. The symbol Au can also mean one atom of gold. So what are atoms and how do we know that substances consist of atoms?

Now that you have completed Section 1, you should be able to do the following things:

Show that you have some idea of what is meant by the terms: 'chemical element', 'symbols for chemical elements'.

Represent elements and atoms of elements using chemical symbols, given access to the information in Appendix 1.

Try SAQ 1 to test your achievement of these Objectives.

SAQ 1 What does the symbol Ne represent?

The answers to the SAQs begin on p. 70.

2 Atoms

2.1 Can atoms be seen?

If you could actually see individual atoms, you would probably accept that atoms exist. Seeing is believing. So can atoms be seen?

The answer to this question depends on what you mean by 'see'. There are theoretical reasons to believe that atoms are too small to be seen by eye, even with the help of the most powerful microscope that uses light, but we shall not go into the reasons here. But there are instruments that do help us to 'see' atoms. Figure 1 shows two pictures obtained by different techniques; in the pictures each small white dot is produced more or less directly by an individual atom.

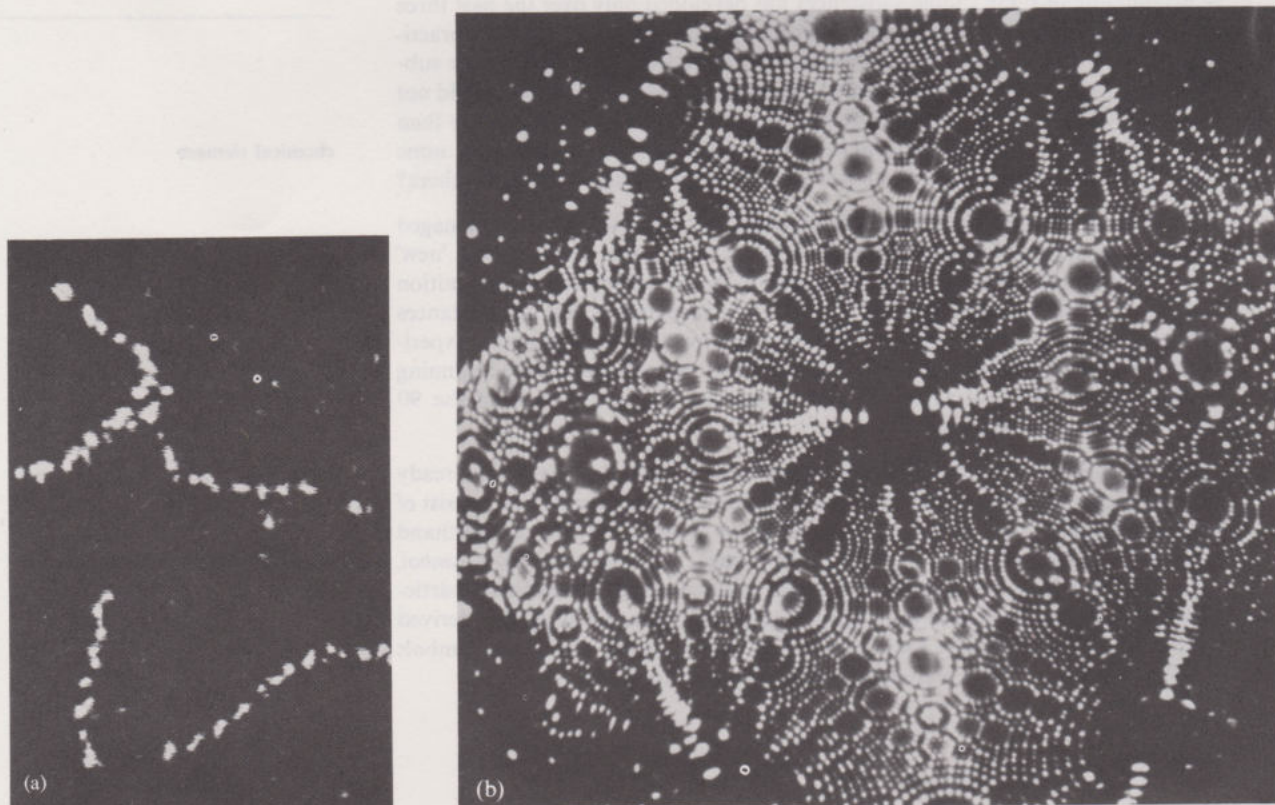


FIGURE 1 (a) Electron micrograph showing thorium atoms; (b) field-ion micrograph of the tip of a tungsten needle.

You may be interested to know how these pictures are produced, although it is not *necessary* to know this at this stage. In fact, we cannot present a satisfactory explanation without some of the ideas that you will meet in Units 29 and 30, but we can give a brief description at this stage.

Figure 1a shows chains of thorium atoms. Thorium is a heavy metallic element. The figure was produced in 1970 using an electron microscope. In principle this instrument is similar to an ordinary microscope, but instead of a beam of light it uses a beam of electrons to illuminate the subject. In Unit 29 you will see that electrons, like photons, sometimes have wave properties. Hence the beam can be focused to allow us to construct a microscope using electron beams instead of light.

Figure 1b is produced by the tip of a very sharp tungsten needle. Tungsten is a hard metal, often used for the filament in electric light bulbs. In Unit 9 you saw how electrons can be emitted from a metal surface when light shines on the metal. If the metal consists of atoms, we might infer from this observation that atoms contain electrons. In fact, electrons can under certain conditions also be transferred from one atom to another, a property that is used in the field-ion microscope. Figure 2 shows how the instrument operates.

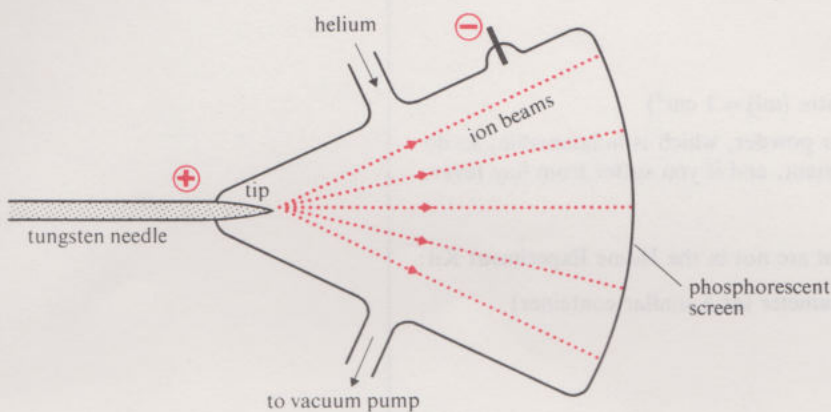


FIGURE 2 Schematic representation of a field-ion microscope.

The tip of the sharp needle of tungsten is given a high positive charge. The opposite (negative) charge is on a screen in front of the needle. The space between the needle and screen is occupied by helium atoms at very low pressure. In this region between the needle and screen a charged object will experience an electrical force. We say that an *electric field* exists in this region, in an analogous way to the existence of a magnetic field in the region around a magnet (Unit 5). So strong is the electric field that electrons transfer from the helium atoms to the atoms in the tip of the needle. This forms positively charged helium atoms. Atoms which have an electric charge are called *ions* (pronounced eye-ons). As they are positively charged, the helium ions are repelled from the positively charged needle and attracted to the negatively charged screen. Notice that the path that they take is along the direction of the field, and that the field radiates from the tip of the needle. So the ions travel radially from the tip to the screen. When an ion hits a point on the fluorescent screen, that point glows; this is similar to the way a picture is produced on a television screen. In the field-ion microscope the pattern of glowing spots that the ions create on the screen is effectively a magnified picture of the tip of the needle. Each spot of light in Figure 1b represents one atom on the surface of the tip of the tungsten needle.

Atoms are obviously very small, so small that the patterns in Figures 1a and 1b are spectacular demonstrations of their existence. At the time of writing, these Figures were the most direct evidence of the existence of atoms, and there are theoretical reasons for supposing that it is not possible to obtain pictures of atoms which are more direct or much clearer. Even so, atoms in these Figures appear as rather blurred blobs, not well defined and certainly without any apparent structure. In these two Units we shall be examining less direct experimental evidence about atoms and their structure. The picture that unfolds is one of remarkable detail and elaborate structure, which is completely hidden in the fuzzy representations in Figures 1a and 1b.

As you might suspect, the investigation of atomic structure is a subject that requires large and expensive apparatus. But there is a very simple experiment for making a rough estimate of the size of atoms, which you can do at home.

2.2 Measuring the size of an atom

You have probably noticed how, on a wet day, oil spreads on a road to produce a thin film, making coloured patterns. Stearic acid is an oily substance, which spreads on water in the same way. For this experiment we shall assume that when stearic acid spreads on water it forms a *monolayer*, a film that is only one atom thick. If you take a known volume of stearic acid, drop it on to water and measure the area, you should be able to estimate the thickness of the layer (volume = area \times thickness). This in turn will give you an estimate of the size of an atom. If our assumption is wrong and the film is several atoms thick (it cannot be less than one atom thick), your result will be an overestimate of the atomic size. So the *true* size of an atom will be equal to or *smaller* than your estimate of the thickness of the layer. In the experiment that follows, we shall assume that atoms are small spheres; the size that you estimate is then a diameter.

Home Experiment 1 The size of atoms

This experiment takes about half an hour to complete, and you will need the following items from the Home Experiment Kit, Part 1:

0.05% stearic acid solution

a dropping pipette

10 ml measuring cylinder (1 millilitre (ml) = 1 cm³)

lycopodium powder (This is a fine powder, which is inflammable, so do not have flames near your experiment, and if you suffer from hay fever, use talcum powder instead.)

You will also need some things that are not in the Home Experiment Kit:

a plastic bowl at least 25 cm in diameter (or a similar container)

a ruler graduated in centimetres

water

Wash the bowl thoroughly with detergent and then rinse it thoroughly with water. Fill it with water until it is nearly full. Set it aside for 5–10 minutes to allow any currents in the water to die away.

While you are waiting, determine the volume of a drop of stearic acid solution. To avoid your having to deal with awkwardly small volumes, the stearic acid is dissolved in light petroleum (0.05 cm³ stearic acid in 100 cm³ of light petroleum). Partially fill the dropping pipette with the solution, and count the number of drops needed to fill the measuring cylinder to the 1 ml (1 cm³) mark.

Number of drops in 1 cm³ =

Now determine the volume of one drop by completing the equation:

$$\begin{aligned}\text{volume of one drop of solution} &= \frac{1 \text{ cm}^3}{\text{number of drops in 1 cm}^3} \\ &= \frac{1 \text{ cm}^3}{\text{ }} = \text{ } \text{ cm}^3\end{aligned}$$

What volume of stearic acid is present in one drop of the solution?

The volume of stearic acid in one drop is the volume of the drop multiplied by the fraction of the solution which is stearic acid (the concentration of the solution).

$$\begin{aligned}\text{volume of stearic acid in 1 drop} &= \text{volume of drop} \times \frac{0.05}{100} \\ &= \text{ } \text{ cm}^3\end{aligned}$$

By now the water should be still. Take the lycopodium powder and dust some on to the surface by shaking it gently out of the tube, holding the tube about 15 cm above the water. You should obtain a thin even scattering over the surface.

Take the dropping pipette and practise dropping one drop into a sink. When you can do this confidently, hold the dropping pipette near the surface of the water above the centre of the bowl. Drop *one* drop on to the surface.

The stearic acid spreads very quickly, pushing the powder aside and forming a thin film. It usually contracts a little as the light petroleum evaporates. Using the ruler, measure the surface covered by the film in various directions, and estimate the area (assume area = average distance²) of the surface that is covered by the film after the light petroleum has evaporated. Enter this result in the first row of Table 2.

TABLE 2 Results of an experiment to determine the size of an atom

Number of drops	Area/cm ²	Area per drop/cm ²
1		
2		
3		

Add a second drop to the middle of the film. Once again estimate the area, and record your result. Repeat the estimate for a third drop. If the film of stearic acid reaches the side of the bowl, you will find it quite difficult to estimate the area because the film will creep around the edge of the bowl.

For each result divide the total area by the number of drops and obtain the area per drop. Write this in the table.

Is the relationship between the total area and the number of drops consistent with the formation of a monolayer?

In our test experiments the value in the third column was roughly constant (within about 25 per cent), suggesting that a layer of constant thickness is formed. If a monolayer is formed, the addition of extra drops of solution would have this effect on the surface area. So the observation is consistent with monolayer formation, but it does not prove that the film is a monolayer.

Now we have to estimate the thickness of the film:

$$\begin{aligned}\text{thickness of film} &= \frac{\text{volume of stearic acid}}{\text{area of film}} \\ &= \frac{\text{cm}^3}{\text{cm}^2} \\ \text{thickness} &= \text{cm}\end{aligned}$$

If the film is a monolayer, this is also your estimate of the size (diameter) of an atom. In SAQ 3 you are asked to estimate the diameter of an atom from the results of this experiment. You should be aware that this experiment provides only a rough estimate because although stearic acid does form a monolayer of particles, the particles of stearic acid contain more than one atom. The layer is therefore one particle thick, but more than one atom thick.

Now that you have completed Section 2.1 you should be able to do the following things:

Describe evidence for the existence of atoms.

Perform and describe an experiment to estimate roughly the size of an atom.

Estimate roughly the number of atoms in an object.

Try SAQs 2 to 4 to test your achievement of these Objectives.

SAQ 2 In what way do the patterns in Figures 1a and 1b suggest the existence of atoms?

SAQ 3 What value of the diameter of an atom do you obtain from your results for Home Experiment 1? Use this value to estimate the magnification in Figure 1b. Assume that the atoms in Figure 1b are touching each other.

SAQ 4 Approximately how many atoms are there in a cup of tea? (Assume that all atoms are roughly equal in size and that the atoms are small cubes which touch each other. Use your answer for SAQ 3 as the length of one of these cubes.)

2.3 Measuring the mass of an atom

Atoms are too small to be seen, even with the most powerful optical microscope. Obviously, they are also too small to be weighed, even with the most sensitive balance. However, we can determine the mass of an individual atom very accurately once we have removed an electron from it.

In the photoelectric experiment in Unit 9, you saw how electrons can be removed from the surface of a metal. If the metal consists of atoms, this experiment suggests that atoms contain electrons. However, an ordinary piece of metal, like any other substance, is not normally electrically charged, so it is reasonable to suppose that the atoms are electrically uncharged or neutral. Yet these neutral atoms appear to emit electrons. As you will discover in several places in these Units, there are various ways of removing electrons from atoms. For example, if atoms are bombarded with a beam of electrons of sufficiently high energy (fast electrons), the atoms may emit some of the electrons which they contain. A fast electron simply knocks an electron out of the atom.

Suppose we bombard the gaseous element neon with a stream of fast electrons so that electrons are knocked out of the neon atoms. We can represent an atom of neon using the symbolism we described earlier.

Write down the symbol for an atom of neon.

Remember that the symbols used to represent an element and an atom of the element are the same. Ne is the symbol for an atom of neon (Table 1).

When an electron is knocked out of a neon atom (normally atoms are electrically neutral) by a fast moving electron, the result is a positively charged atom. We call atoms that have either a positive or negative electric charge *ions*. Again we can represent ions using symbols to show which atom produced the ion and to show the charge on the ion. A neon atom that has lost one electron is represented by Ne^+ . (If one negative charge is taken from the neon atom, this leaves the atom with a net positive charge—hence the symbol Ne^+ .) Most atoms, it is found, can lose more than one electron; thus an atom of neon that has lost two electrons is represented by Ne^{2+} . Notice that the unit of electric charge in this symbolism is the charge on the electron (— for the electronic charge, + for the opposite charge).

ions

If the symbol e^- is used to denote the electron, what event does this collection of symbols represent?



This merely states that when a fast electron (e^-) collides with an atom of neon (Ne), an electron is knocked out of the atom; the result is a positive ion of neon (Ne^+) and two electrons. Notice that it is quite correct to describe equation 1 as an *equation*, and we have used the 'equal to' sign to indicate that the things on the left-hand side produce the things on the right. The number of atoms and of electric charges on each side is equal. We say that the equation *balances*. Later, in Unit 12, you will have opportunities to gain practice at balancing equations.

balanced equation

Now that you know how to represent ions, we can proceed with the method of measuring their masses. The instrument used is a mass spectrometer. Although the mass spectrometer strictly measures or compares the masses of *ions*, we normally consider it to provide values of *atomic* masses. The reason for this is that

the mass of an electron is almost insignificant in comparison with the mass of an atom, as we show in TV 10. So, for the remainder of this discussion we shall talk about the mass of an atom.

2.3.1 The mass spectrometer

Suppose that ions are produced in a gas containing atoms of two different masses by bombarding atoms with electrons. In Figure 3 the ions of different masses are represented by circles of different sizes. The gas is contained between two metal plates. If the plates are momentarily connected to a source of electrical energy, a short pulse of electricity is induced on the plates as shown in Figure 3, one plate being positive the other plate negative. We then say that there is a difference in the voltage or in the *electric potential* between the two plates. We shall use the term electric potential in preference to voltage in these Units.

electric potential

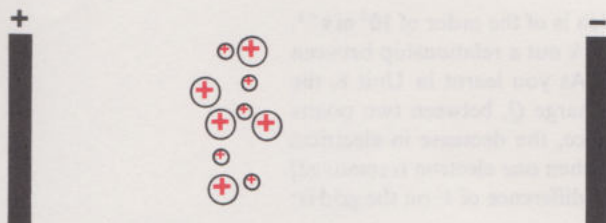


FIGURE 3 Positively charged ions between charged plates.

What would happen to the ions between the plates?

Being positively charged, the ions are repelled by the positively charged plate and attracted by the negatively charged plate.

What determines the force on the ions when the plates are pulsed with the electric potential?

In Unit 8 you learnt that negatively charged objects, for example electrons, travel towards the positive terminal of a battery because their energy is lower at that terminal. The electrical force is determined by the charge on the electron, or in our case on the ions, and the potential difference between the plates. In effect, the electric pulse gives the ions a kick like you might kick a football. Now the speed of the football depends on how hard you kick it. If the ions have each lost only one electron, their charges are all equal and the kick given by the electric pulse is the same for all ions. But is their speed the same? If you can imagine kicking a football made of lead, you will realize that the heavier ions travel more slowly than the lighter ions as a result of the electric pulse.

The simplest of many ingenious devices uses only this principle to sort the ions into groups containing ions of the same mass. It is called a time-of-flight *mass spectrometer* and is shown in Figure 4. (In TV 10 you see a more conventional and modern instrument, which uses a different principle to separate the ions.) Follow the diagram (Figure 4) of the time-of-flight mass spectrometer from points 1 to 8.

mass spectrometer

Notice that the apparatus is evacuated (the air and any other gases present are pumped away) to ensure that only the gas in the sample is ionized and that the electrons and ions can travel without colliding with gas atoms except in the ion source.

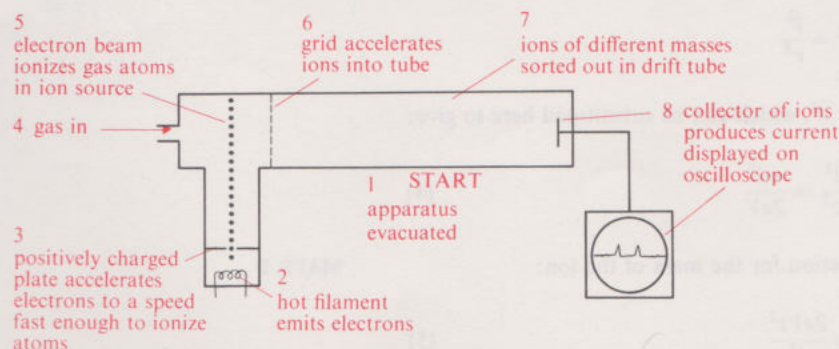


FIGURE 4 Schematic representation of a time-of-flight mass spectrometer.

An electron beam is produced by heating a filament (a metal wire) in the evacuated ion source—another way to produce electrons! Effectively, the electrons are ‘shaken’ out of the wire by heat energy (see Unit 8). The metal grid is a charged plate, which is designed to let the accelerated ions pass through into the drift tube, where they sort themselves out according to their masses. Figure 5 shows how pulses containing ions of three different masses get sorted as they drift towards the collector.

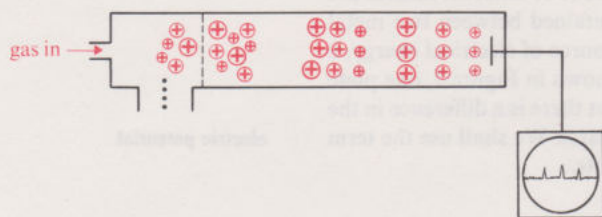


FIGURE 5 Pulses of ions in the mass spectrometer sorting according to their mass; the lighter atoms travel faster. Different masses are represented by circles of different radii.

Evidently, the velocity of the ions in the tube, which is of the order of 10^5 m s^{-1} , depends on their mass, and it is not difficult to work out a relationship between the velocity (or the time of flight) and the mass. As you learnt in Unit 8, the difference in electrical energy of an object with charge Q , between two points separated by a potential difference V , is QV . Hence, the decrease in electrical energy of an ion with a charge $+e$ (the net charge when one electron is removed) after it has been accelerated by an electric potential difference of V on the grid is:

$$E_{el} = eV$$

When this ion enters the tube its velocity is v . If its mass is m , write an expression for its kinetic energy.

The expression for its kinetic energy is

$$E_k = \frac{1}{2}mv^2$$

Now this kinetic energy is the result of the acceleration of the ion towards the grid in the mass spectrometer.

How can the velocity be expressed in terms of e , V and m ?

Since the gain in kinetic energy is equal to the loss of electrical energy, we can write

$$E_k = E_{el}$$

Hence

$$\frac{1}{2}mv^2 = eV \quad (2)$$

Equation 2 can easily be rearranged by multiplying both sides by $2/m$:

$$v^2 = \frac{2eV}{m} \quad (3)$$

If the drift tube has a length l , the time t for an ion to travel the length of the tube (time of flight t) is l/v , so

$$t^2 = \frac{l^2}{v^2}$$

Equation 3 contains an expression for v^2 , which can be substituted here to give:

$$t^2 = \frac{l^2}{v^2} = \frac{ml^2}{2eV} \quad (4)$$

We can rearrange this to get an expression for the mass of the ion:

$$m = \frac{2eVt^2}{l^2} \quad (5)$$

Unit 8, Section 6.3

MAFS 2

Equation 4 shows how ions of different mass take different times to travel along the tube, a conclusion we also reached by appealing to everyday experiences. Equation 5 enables us to calculate the mass of the ion, if the quantities on the right-hand side are known.

What experimental data do you need to know, apart from those which are fixed by the construction of the mass spectrometer, or measured by it, to enable you to calculate the mass of an ion?

The electric potential difference, V , and the length, l , are fixed by the mass spectrometer, and the time, t , is measured by it. Only the electronic charge, e , needs to be known. In TV 10 you see how the electronic charge can be measured experimentally. The value obtained is

$$e = 1.602 \times 10^{-19} \text{ C}$$

With this information and the results of a mass spectrometry experiment, you should be able to determine the mass of an atom, using equation 5.

In an experiment to measure the mass of an atom of sodium, the following conditions were used:

$$V = 200 \text{ volts}$$

$$l = 0.4 \text{ metre}$$

A single peak was found in the mass spectrum and the corresponding time of flight was $t = 9.76 \times 10^{-6} \text{ s}$.

You now have all the data that you need to determine the mass of an atom of sodium.

What is the electrical energy lost by a sodium ion as it accelerates out of the ion source into the drift tube?

This energy is $E_{el} = eV$

$$= (1.602 \times 10^{-19} \text{ C}) \times (200 \text{ V})$$

$$= 3.204 \times 10^{-17} \text{ J}$$

Remember from Unit 8 that $1 \text{ joule (J)} = 1 \text{ volt} \times 1 \text{ coulomb}$
 $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$

Equation 5 should now provide a value for the atomic mass:

$$m = \frac{2 \times (3.204 \times 10^{-17} \text{ kg m}^2 \text{ s}^{-2}) \times (9.76 \times 10^{-6} \text{ s})^2}{(0.4 \text{ m})^2}$$

$$= 3.815 \times 10^{-26} \text{ kg}$$

This mass is obviously *very* small, and not a convenient value to use in calculations. For this reason, scientists often express the mass of an atom relative to the mass of another atom. It would seem sensible to choose as a reference the lightest atom, hydrogen, and set its relative mass equal to 1. In fact hydrogen was originally chosen as the reference atom, but it has proved to be more convenient to use as reference a particular atom of carbon with almost exactly twelve times the mass of an atom of hydrogen. To keep the relative mass of a hydrogen atom conveniently near to unity, the relative mass of the atom of carbon is set at exactly 12. The *relative atomic mass* (A_r) of an atom X is defined as twelve times the ratio of the mass of the atom X to the mass of the carbon atom chosen as reference. The relative atomic mass of sodium turns out to be 22.99.

relative atomic mass, A_r

In addition to providing a means of determining atomic masses very accurately, mass spectrometry provides a method of examining mixtures of atoms of different masses, as Figure 5 shows. This facility produced a surprising result when the mass spectrum of the element neon was first obtained. Neon can be separated from the other components of the atmosphere and obtained in very high purity by a process known as distillation. When very pure neon is obtained in this way, it gives the mass spectrum shown in Figure 6.

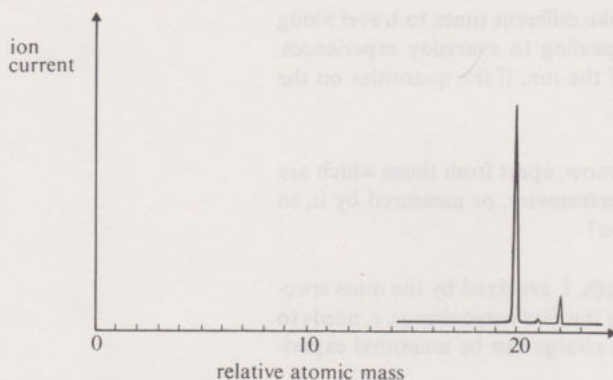


FIGURE 6 Mass spectrum of neon. The heights of the peaks give the relative abundances of the isotopes.

relative abundance

What do you notice about Figure 6?

First you are probably surprised to find that for neon there are *three* peaks instead of the *one* peak found for sodium. Intuitively, you might expect that an element would contain only one kind of atom, but evidently the mass of an atom is not quite so characteristic. The most plausible explanation is that neon consists of three different types of atom, which are distinguished by their mass. Atoms of an element which differ in their masses are called *isotopes* of the element. Thus, neon has three isotopes. On the other hand, sodium gives a mass spectrum that has only one peak: sodium consists of one isotope. So do other elements consist of mixtures of isotopes?

It turns out that most of the elements do. For example, Figure 7 shows the mass spectra of magnesium and copper.

Now examine the relative atomic masses of the isotopes that have been mentioned so far in this discussion. What do you notice about them?

The most striking thing is that the relative atomic masses are whole numbers or at least very close to whole numbers. The probability that this is due to pure chance is so small that it can be discounted. It seems to suggest that atoms consist of common structural units. The relative atomic mass of hydrogen is very close to one, so atoms appear to consist of particles that have masses about equal to the mass of a hydrogen atom. Another noticeable feature of the values is that they are not *exactly* whole numbers. Nor is it possible to multiply them by some factor to bring them exactly to whole numbers. Although these differences may seem quite small, they have far-reaching significance. You will see later that they are related to the energy that is released in the reactions occurring in the Sun, in nuclear bombs and in nuclear power stations. For the moment we shall concentrate on the more obvious feature of the masses of isotopes, their proximity to integers, which suggests that atoms consist of some fundamental particles.

Can you suggest a way of testing whether all atoms consist of the same particles?

If atoms do consist of the same particles, every isotope should have a relative atomic mass close to a whole number. Perhaps the suggestion could be tested by determining the relative atomic masses of *all* isotopes: if a number of elements have isotopes with relative atomic masses that are awkward fractions, then the suggestion is certainly disproved.

So far you have been given the relative atomic masses of isotopes of carbon, neon, sodium, magnesium and copper. In fact, every known isotope has been found to have a relative atomic mass that is very nearly a whole number. It therefore appears that atoms in general do consist of some fundamental particles of similar mass to the mass of a hydrogen atom with relative atomic mass of about 1. Later in these Units we shall consider why this should be.

If you want to refer to a particular isotope of an element, you simply specify the relative atomic mass rounded to the nearest whole number. This whole number is called the *mass number*, A , of the isotope. Thus, the three isotopes of neon are

isotope

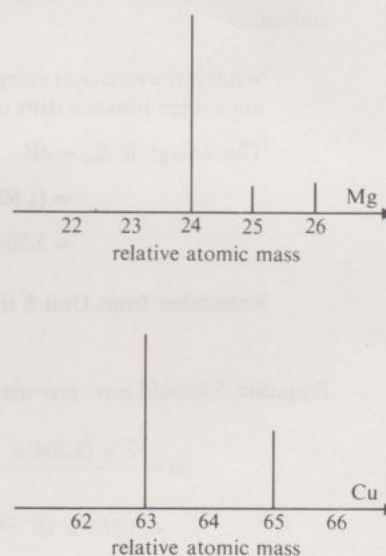


FIGURE 7 Mass spectra of magnesium and copper.

mass number, A

represented by the symbols ^{20}Ne , ^{21}Ne and $^{22}\text{Ne}^*$. To get accurate values of relative atomic masses you then look up the isotope in a table such as you can find in the Data Book.

Almost all elements occur naturally as mixtures of isotopes. Carbon, the reference substance for relative atomic masses, is itself a mixture of three isotopes. The most common one is the 'standard' isotope ^{12}C , and this is accompanied by about 1 per cent of ^{13}C and very small amounts of ^{14}C . This is why we carefully referred to a 'particular atom' of carbon when we defined it as the standard for the relative atomic mass scale.

Chemically, it is not usually possible to distinguish between the different isotopes of an element. They differ in mass but have the same chemical properties. Consider soot, which is mainly graphite, a form of carbon. ^{12}C soot is chemically the same as ^{13}C or ^{14}C soot!

Since we usually work with substances that consist of a mixture of isotopes, the relative atomic mass of this mixture is therefore important. This is determined by the atomic masses of the isotopes present and by their relative amounts. For example, neon contains 90.9 per cent ^{20}Ne , 0.26 per cent ^{21}Ne and 8.8 per cent ^{22}Ne . To calculate the relative atomic mass of the *element* (the mixture of isotopes), you simply multiply each isotopic mass by the relative abundance of the isotope and add the products. Thus, the relative atomic mass of neon is:

$$A_r = (19.99 \times 0.909) + (20.99 \times 0.0026) + (21.99 \times 0.088)$$

$$A_r = 20.2$$

A table of accurate relative atomic masses of the elements is given at the end of these Units in Appendix 1. If you examine this, you will find that several elements have relative atomic masses which are close to whole numbers. The reason for this is that these elements consist largely of only one isotope. Other elements have relative atomic masses that are not nearly integral, indicating that they consist of a mixture of isotopes.

2.4 Summary of Section 2

In the following Sections of these Units we shall examine the internal structure of atoms. So at this stage it is useful to summarize the discussion so far.

- 1 All substances consist of one or more of the ninety or so naturally occurring simple substances called *elements*.
- 2 Matter is composed of *atoms*, which are too small to be seen, but which can be 'photographed' by certain techniques, for example the field-ion microscope or the electron microscope.
- 3 Atoms are represented by symbols, which are also used to represent elements.
- 4 The size of an atom can be determined roughly by measuring the area of a substance that spreads on water to produce a monolayer. The result gives the diameter of an atom as 10^{-9}m . This value is actually an overestimate; the diameter of an atom is actually close to $3 \times 10^{-10}\text{m}$.
- 5 Atoms apparently contain electrons, since in forming ions they lose electrons. The masses of atoms can be measured precisely using a mass spectrometer. In one form, the time-of-flight mass spectrometer, the ions are accelerated using an electric field, and the time they take to travel a fixed distance is measured. Typically, the mass of an atom is about 10^{-26}kg .
- 6 Rather surprisingly, it is found that most elements do not consist of atoms which all have identical masses. Apparently, elements are not characterized by atomic mass. Atoms of the same element but of different mass are called *isotopes*. The relative masses of isotopes, using an isotope of carbon as standard, are very close to whole numbers. This suggests that atoms consist of fundamental particles. We denote isotopes of an element by using the *mass number*, the whole number closest to the relative atomic mass, for example ^{12}C , ^{20}Ne , ^{22}Ne .

* These terms are spoken as 'neon twenty', 'neon twenty-one', and 'neon twenty-two'.

Now that you have completed Section 2, you should be able to do the following things:

Show that you have some idea of what is meant by the terms: 'ion', 'mass spectrometer', 'balanced equation', 'relative atomic mass', 'isotope', 'mass number', 'electric potential', 'relative abundance'.

Represent elements, atoms, isotopes and ions using symbols.

Describe and interpret an experiment in which atomic masses can be measured.

To test your achievement of the above Objectives, try the following SAQs.

SAQ 5 What does the symbol Hg^+ mean?

SAQ 6 The mass spectrum of mercury is shown in Figure 8. Why are several peaks observed in the spectrum?

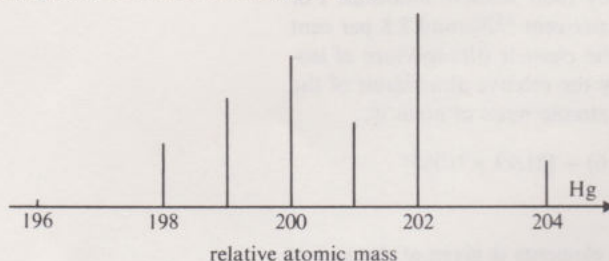


FIGURE 8 Mass spectrum of mercury.

SAQ 7 Write symbols for each of the isotopes of mercury which give rise to the peaks in the mass spectrum in Figure 8.

SAQ 8 The relative atomic mass of the element chlorine is 35.45. Suggest a reason why it is not close to a whole number.

3 Atomic structure—the nuclear model

Although we have told you quite a lot about atoms, you probably realize that many questions are raised by the discussion so far. For example, we have not considered where the electrons are in an atom. If atoms contain electrons, they also contain positive charges to keep them electrically neutral, so there are positive charges to account for as well. Nor have we considered whether the mass of an atom is spread uniformly throughout its volume. Some of the answers to these questions came from a series of experiments performed in 1910 by Ernest Rutherford and his group of physicists at Manchester. The picture of the atom that emerged from these experiments is still basically the same as the one we use today. But before we examine Rutherford's experiments and conclusions, a word of warning.

As you have seen in earlier Units, explanations of scientific observations often involve the construction of models. As science progresses through new experiments, old models become refined or rejected in favour of new models to accommodate the new facts. The model of the atom that we shall develop in these Units is not a final one, nor does it account for all the experimental facts that are known. However, it has the attractions of simplicity and usefulness; with it, we can interpret and often predict a wide range of facts. In particular, as you will discover in Unit 13, the chemical behaviour of elements depends strongly on their atomic structure.

These are sufficient reasons for us to explore atomic structure and to limit the model in the way we have. Where it does have limitations we shall point these out, and towards the end of the Course you will see how these limitations are overcome by more sophisticated models.

3.1 The α -particle experiment and the Rutherford atomic model

As you saw in Figure 1, the best pictures we have of individual atoms show them as fuzzy dots. Their structure is not revealed. To probe the structure of the atom, more subtle experiments are required. Much of the information on atomic structure is inferred from the interaction of light with atoms and of particles with atoms.

Some of the heavier elements are unstable. It had been known since 1896 that elements such as uranium and radium emit radiation and particles of various types. We shall have more to say about this phenomenon shortly. Radium, for example, emits α -particles, which in earlier experiments, Rutherford had identified as helium atoms that had lost two electrons and were thus positively charged. (This experiment is discussed in Radio 05.)

α -particle

What is the symbol for an α -particle which shows that it is a helium ion?

The symbol is that for a helium atom with two positive charges, He^{2+} .

Rutherford also determined that they are shot out of the radium with very high speed, more than 10^7 m s^{-1} . However, in air they quickly slow down and stop in only a few centimetres. This is hardly surprising when you consider how many atoms the α -particle would collide with when it travels that distance. From the density of air and atomic sizes and masses it is possible to estimate that an α -particle would collide with about 100 000 atoms in a few centimetres. In fact, you might be surprised that it travels so far. This penetration of atoms by α -particles seems to suggest that atoms are certainly not solid lumps of matter like minute billiard balls.

Rutherford saw in these α -particles the opportunity to probe the structure of the atom. In the experiment he devised, a stream of α -particles was shot at a thin film of gold foil, and the scattering of the α -particles in various directions was observed. Figure 9 shows an outline of the apparatus.

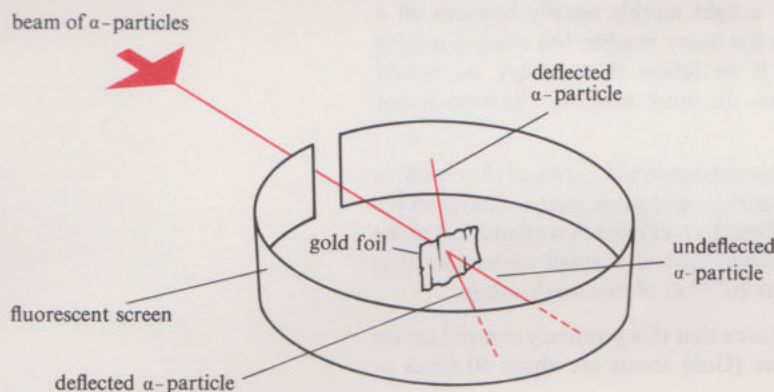


FIGURE 9 Deflection of α -particles in Rutherford's gold foil experiment.

A small piece of radium embedded in a lead container emitted a stream of α -particles. Remember that air stops α -particles, so the experiment had to be done in a vacuum. The α -particles entered the evacuated chamber and hit a piece of thin gold foil. The foil was a few micrometres (10^{-6} m) thick.

If you assume that the atoms in gold foil touch each other and that the diameter of an atom is about 10^{-10} m , how many atoms thick was the foil?

The thickness of foil (10^{-6} m) divided by the atomic diameter (10^{-10} m) gives about 10 000 layers of atoms in the foil.

When an α -particle struck the fluorescent screen, it produced a flash of light on the screen. By watching for the flashes, Rutherford and his colleagues were able to determine the number of α -particles scattered at various angles from the foil.

Knowing that α -particles travel a few centimetres in air before they are stopped, what would you expect the result of Rutherford's experiment to be?

With even fewer atoms in their path in the evacuated chamber than in a few centimetres of air, the α -particles might be expected mainly to pass through the gold foil, perhaps with a little spreading of the beam. In fact, most of the α -particles did pass through the foil, largely undeflected.

Does this observation confirm the suggestion drawn from the range of α -particles in air?

Since nearly all of the α -particles appear to *pass through* a thickness of about 10 000 atoms *without deflection*, it seems that atoms consist largely of empty space. So where is the mass of the atom situated, and where are the electrons in the atom and the corresponding positive charges? By patient observations, Rutherford and his colleagues obtained the results that told them about the internal structure of the atom.

Occasionally, they found that an α -particle was deflected through a very large angle, back towards the source. So although most of the particles passed almost straight through the foil, some rebounded as if from a head-on collision with something immovable. As Rutherford said in 1936*, 'It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.'

Faced with this curious result, Rutherford quickly established a model of the atom that would explain the scattering experiments. Obviously, the α -particles that are scattered backwards are acted on by a very powerful force.

Can you suggest what type of force this is? Remember that α -particles (He^{2+}) carry a positive charge.

Atoms, as you know, contain electrons, and to preserve neutrality they must also contain positive charges. It seems likely that the force between the atom and the α -particle is an electrostatic force (Unit 8). But electrons are also very light; the mass of an electron is much smaller than the mass of an α -particle. If you have ever played marbles, you will know that a light marble usually bounces off a heavy one without having much effect on the heavy marble, but a heavy marble will knock a light one out of its path. If we follow this analogy, we would decide that in a collision with an electron, the more massive α -particle is not likely to rebound.

Rutherford assumed, correctly, that the rebound occurred because of the repulsive force between the positive charge of the α -particle and some *positive* charge in the atom. To experience a sufficiently strong force, he reckoned that all or most of the positive charge in the atom must be concentrated at a small centre and that the α -particle must approach within about 10^{-14} m of this small centre.

From the analogy with marbles, it also follows that this positively charged centre must carry most of the mass of the atom. (Gold atoms are about 50 times as massive as α -particles.)

It is not difficult to see how Rutherford devised a model to explain his experiments. He proposed that nearly all of the mass and all of the positive electrical charge are concentrated into a small centre in the atom, the *nucleus*. Using this nuclear model of the atom, the interaction of a beam of α -particles and a thin foil (layers of atoms) can be pictured by the paths shown in Figure 10.

nucleus

Most of the α -particles pass through the foil undeflected, but sometimes an α -particle is deflected, occasionally through a large angle. The average deflection is less than 1° , and only about 1 in 20 000 α -particles is deflected through 180° .

Figure 10 depicts the nuclei of atoms as small centres, but even so, it exaggerates the size of the nuclei. Rutherford was able, from his scattering experiments, to estimate the size of a nucleus. The value that he estimated was less than 10^{-14} m in diameter. The rest of the atom (diameter of about 10^{-10} m) must contain very little mass and all the negative charge of the atom. Notice that the nucleus is only a tiny part of the volume of the atom. The atom as a whole is 10^4 times as big as its nucleus!

* Ernest Rutherford, Lecture at Cambridge, 1936, in *Background to Modern Science*, eds J. Needham and W. Pagel, Cambridge University Press (1938).

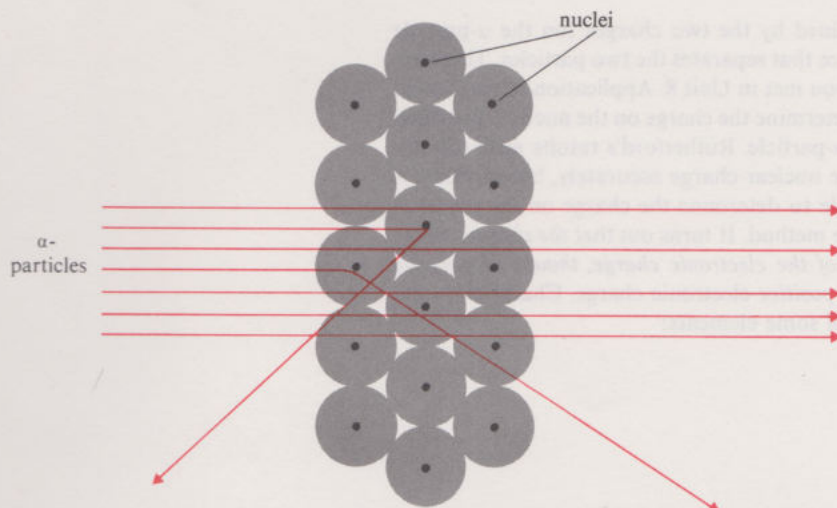


FIGURE 10 Scattering of α -particles by atomic nuclei.

Imagine that you scale up an atom to fit into a large football stadium, perhaps 300 m in diameter. How big would the nucleus be?

A factor of 10^{-4} gives the nucleus a diameter of a few centimetres—no bigger than a golfball.

Can you suggest what the negative charge might be in the vast empty regions between nuclei?

Rutherford supposed that the negative charge must be electrons circulating the positively charged nucleus.

The *nuclear* or *Rutherford model* of an atom with one electron, pictures it as in Figure 11, much like a minute model of the Earth orbiting the Sun; in this model the atom is depicted as being nearly all empty space.

The model of the atom illustrated in Figure 11 has the attraction of simplicity and is also satisfactory for explaining the scattering of α -particles. However, it soon became necessary to refine this model. According to the theories of electromagnetic radiation, an electron orbiting the nucleus, as Figure 11 shows, would continuously lose energy and quickly spiral into the nucleus. The fact that this does not happen indicates that such a simple model is incorrect. As you will find out in Section 5, electrons cannot be adequately described as particles similar to billiard balls or marbles. Electrons in atoms cannot have sharp, well-defined orbits. So where is the electron in the atom? As you will discover in Unit 30, quantum theory tells us that it is impossible to answer that question precisely. What the theory does say is that if you were able (which you are not) to take a large number of photographs of an atom containing one electron, by superimposing these photographs you would obtain an impression of where the electron spends most of its time. The result of such a theoretical prediction is the distribution shown in Figure 12. Each small dot represents one instantaneous picture of the electron.

Figure 12 is itself a simplification. Since the Figure is restricted to the two dimensions of the page, it fails to show the complete prediction of the theory; that the region occupied by the electron is three-dimensional and spherical. This new description of the electron's 'path' is called an *orbital*. The orbital shown in Figure 12 has spherical symmetry, by which we mean that the probability of finding the electron at a given distance from the nucleus is the same in all directions. However, this is not true for all atoms. The shapes of orbitals in atoms that contain several electrons are often more complicated and not spherical.

This failure to provide a completely accurate model of the electron in the atom does not belittle Rutherford's experiments and interpretation. There is no doubt that the α -particle scattering experiment provided more information about atomic structure than any other single experiment. And in fact, the results of α -particle studies were to provide yet more information about the nucleus.

If the force that repels the α -particles is an electrostatic one, what factors affect the angle of deflection (or the magnitude of the force)?

Rutherford atomic model

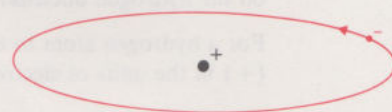


FIGURE 11 Rutherford's planetary model of the hydrogen atom.



FIGURE 12 The 'uncertain' model of the hydrogen atom.

orbital

Electrostatic interactions are determined by the two charges (on the α -particle and on the nucleus) and by the distance that separates the two particles. These are related by the Coulomb law, which you met in Unit 8. Application of this law to the experiment should enable us to determine the charge on the nucleus, provided we already know the charge of the α -particle. Rutherford's results were too imprecise to allow him to determine the nuclear charge accurately, but in 1920 his co-worker, James Chadwick, was able to determine the charge on the nuclei of several different elements by the same method. It turns out that *the charges on the nuclei are exactly integral multiples of the electronic charge, though of opposite (positive) sign*. Expressed in units of *positive* electronic charge, Chadwick found the following charges on the nuclei of some elements:

Cu 29+
 Ag 47+
 Ir 77+
 Au 79+

In a gold foil, as used in Chadwick's experiments, there are millions of nuclei, each with the same positive charge of 79 units.

How is it that the foil as a whole does not have an electric charge?

The only explanation is that the positive charge on each nucleus is *exactly* compensated by the negative charge carried by the electrons. Thus, each gold atom is electrically neutral and must have 79 electrons to balance the 79 positive charges on the nucleus. Similarly, an atom of copper has 29 positive charges on its nucleus and 29 electrons circulating in the space surrounding the nucleus. So *atoms* of each element are uniquely described by a single number known as the *atomic number* and denoted by Z . This number is equal to the number of electrons surrounding the nucleus and is also equal to the number of positive charges on the nucleus.

atom
 atomic number, Z

A hydrogen atom has one electron. What charge would you expect to find on the hydrogen nucleus?

For a hydrogen atom to be neutral, the charge on its nucleus must be $+e$ ($+1$ in the units of electronic charge.)

A smaller positive charge than $+e$ has never been found. Since the charges on nuclei of other atoms are integral multiples of the charge on the hydrogen nucleus (according to Chadwick's experiments), it can be reasonably assumed that each atomic nucleus contains as many hydrogen nuclei as the number of positive charges on the nucleus. A nucleus of copper would contain 29 hydrogen nuclei, a nucleus of silver would contain 47, and so on. A hydrogen nucleus, H^+ , can be regarded as a building block (an elementary particle) in the construction of other nuclei. This elementary particle is given the name *proton* and a symbol 1_1p , where the subscript denotes the charge ($Z = 1$, the atomic number) and the superscript denotes the mass number*.

proton

Do all other nuclei consist only of protons? If you refer to Figure 6, the answer should be obvious.

Figure 6 shows that there are three different isotopes of neon, all with the same atomic number ($Z = 10$) but with different mass numbers (20, 21 and 22).

How many protons are there in a nucleus of neon?

There are 10; to balance the 10 negatively charged electrons in a neon atom, the nuclear charge must be $+10$.

What is the contribution of ten protons to the atomic mass?

Ten protons can only account for ten units of mass in a neon nucleus. There must, therefore, be other inhabitants of a neon nucleus, and these must contribute to its

* Often the symbol p (without indices) is used to denote the proton, and similarly other letters are also used without indices to denote other particles, for example, α and e .

mass but not to its charge.

Can you suggest what the mass of these other components of the nucleus might be? (Compare the mass numbers of the neon isotopes.)

The isotopes of neon differ by mass numbers of one and two. We can conclude from this that whatever the neutral component of the nucleus is, it has a mass of one unit of atomic mass. It seems likely that this neutral component is another elementary particle, of similar mass to the proton but without charge. This particle is given the name *neutron* and the symbol ${}_0^1\text{n}$. Again the subscript denotes the charge (zero) and the superscript indicates the mass number of the particle.

neutron

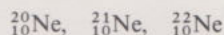
It is important to appreciate that the existence of the neutron was deduced by the reasoning outlined here, based on comparisons of atomic numbers and mass numbers. Experimental evidence that neutrons actually exist came several years later when in 1932 Chadwick produced neutrons.

All nuclei are composed of protons and (with the exception of a hydrogen nucleus) neutrons. The *atomic number* is the number of protons in the nucleus.

How is the *mass number* related to the numbers of protons and neutrons in a nucleus?

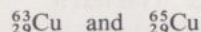
The mass number is the *sum* of the numbers of protons and neutrons. Remember that they both have a mass number of 1.

Sometimes it is useful to represent atoms using symbols that show both the mass number and the atomic number, and hence the number of protons and neutrons in the nucleus. For example, an atom of neon contains ten protons, so the three isotopes can be represented by the symbols:



Copper consists of two isotopes with relative atomic masses very close to 63 and 65. Write symbols to represent these two isotopes, showing the atomic numbers and mass numbers. A copper nucleus has a charge of +29.

The symbols are



The mass number is simply the whole number closest to the relative atomic mass (that is, the number of protons plus neutrons); and the atomic number is the number of protons (equal to the positive nuclear charge).

How many neutrons are in each of the two isotopes of copper?

The number of neutrons is merely the difference between the mass number and the number of protons:

For ${}_{29}^{63}\text{Cu}$, $63 - 29 = 34$ neutrons.

For ${}_{29}^{65}\text{Cu}$, $65 - 29 = 36$ neutrons.

A full list of elements and their relative atomic masses arranged in alphabetical order is given at the end of these Units in the Table in Appendix 1. Inspect the Table in Appendix 1 and compare the numbers of neutrons and protons in the elements. For a rough comparison, take the relative atomic masses of *elements* and ignore the existence of isotopes.

What do you notice about the relative numbers of neutrons and protons?

For all of the elements except hydrogen and helium, the relative atomic mass is more than double the atomic number, but only a little more for the light elements. This observation can be interpreted by saying that nuclei generally contain more neutrons than protons. This is a useful generalization because it helps to provide rough values of the numbers of protons and neutrons in a nucleus if you know the relative atomic mass.

3.2 Summary of Section 3

1 The Rutherford experiment on the scattering of α -particles shows that atoms consist of a positively charged nucleus of about 10^{-14} m in diameter, in which the great majority of the mass of the atom is concentrated. The region around the nucleus (diameter about 3×10^{-10} m) contains the electrons.

2 The nucleus consists of protons (of mass 1 and charge +1) and neutrons (of mass 1 and zero charge).

3 The atomic number, Z , is the number of protons in the nucleus, which equals the number of electrons in the atom.

4 The mass number, A , is the sum of the numbers of protons and neutrons in the nucleus.

Now that you have completed Section 3 you should be able to do the following things:

Show that you have some idea of what is meant by the terms: 'Rutherford atomic model', ' α -particle', 'nucleus', 'orbital', 'atom', 'atomic number', 'proton', 'neutron'.

Represent the numbers of protons, neutrons and electrons in an atom using symbols.

Describe the Rutherford model of the atom, giving roughly the dimensions of the atom and the nucleus, and describe how evidence for the model was obtained.

To test your achievement of these Objectives, try the following SAQs.

SAQ 9 What do the symbols ${}^1_1\text{H}$, ${}^2_1\text{H}$ and ${}^3_1\text{H}$ represent?

SAQ 10 Which particular observations in the Rutherford experiment indicated that the atom contains a small heavy nucleus, with a positive electrical charge?

SAQ 11 Complete the table in the margin without reference to the text if possible. (You may assume that on the relative atomic mass scale, the mass of the electron is zero.) Remember that the α -particle is a helium nucleus.

SAQ 12 Platinum consists of four isotopes with relative atomic masses close to 194, 195, 196 and 198. Chadwick found that for platinum, $Z = 78$. Using this value of Z for platinum, write symbols for these isotopes.

Particle	Mass number	Charge
proton		
neutron		
H atom		
α -particle		
electron		

4 Radioactivity and nuclear reactions

4.1 Radioactivity

In his experiments on atomic structure, Rutherford used the element radium as a source of α -particles.

If a radium atom emits an α -particle, what happens to the mass number and atomic number of the radium atom?

Remember that an α -particle is a helium nucleus, represented by the symbol ${}^4_2\text{He}^{2+}$, so that the mass number is reduced by four, and the atomic number is reduced by two. The product has a different atomic number: it is no longer radium!

The emission of an α -particle by a radium atom is one example of a *nuclear reaction*, which are the subject of this Section. It leads us to examples of the dating of archaeological specimens, reactions in stars, nuclear power stations and the synthesis of new elements.

nuclear reaction

As we stated at the beginning of these Units, there are about 90 elements which

occur naturally. Uranium (with atomic number 92) is the heaviest of these, and, as you may know, it is not absolutely stable. All elements with atomic number larger than 92 are unstable. Atoms of these heavy elements tend to break up spontaneously or *decay* to lighter elements. In doing so they emit radiation, sometimes α -particles and sometimes other types of radiation known as β -particles and γ -rays. We shall now consider the three types of radiation in turn.

radioactive decay

4.1.1 α -Radiation

As you know, α -particles are helium nuclei. We can represent an α -particle by the symbol ${}^4_2\text{He}$. An example of α -emission is the decay of an isotope of uranium shown in equation 6:



This particular decay happens to be very slow, which, as you will discover in Unit 26, is a useful feature.

Notice that, as you anticipated, the atomic mass and the atomic number are both reduced and that the product is *not* uranium but the element thorium. Notice too that equation 6 'balances': the mass number (protons + neutrons) on the left (238) is equal to the mass number (234 + 4) on the right; the total charge on the nuclei on the left (92) is equal to the total charge on the nuclei on the right (90 + 2).

This balancing of mass and charge is important in nuclear processes, and although you might reasonably assume that mass does not change in a reaction of the type shown in equation 6, in fact mass does not usually balance *exactly* in nuclear processes. However, the total *number* of particles (protons plus neutrons) does not change. At the end of the Course, in Unit 30, we shall consider in more detail the energy changes involved in nuclear reactions. And in Unit 32, the possible environmental consequences of converting the energy stored in nuclei will be examined. Here we shall simply note that small changes in the total mass result in enormous energy changes. Remember that the relative atomic masses of atoms are *not* exactly whole-number multiples of the masses of some simple fundamental particles such as protons and neutrons.

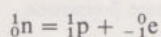
4.1.2 β -Radiation

β -particles are electrons that are emitted from the *nucleus* of an atom, often with high speed, sometimes close to the speed of light. We can represent a β -particle by the symbol β^- (or by ${}^0_{-1}\text{e}$, since it is just a fast electron: the electron has nearly zero mass, about 1/1800 the mass of a hydrogen atom; hence the β -particle has a mass number of zero, and a charge of -1).

β -particle

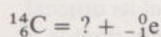
What effect would you expect the emission of one β -particle from a nucleus to have on the nucleus? (Estimate the effect on the mass and charge of the nucleus.)

The mass number will remain the same because the electron has nearly zero mass. However, the emission of one negative charge by the nucleus increases its *positive* charge by one. In fact, in the emission of a β -particle, one neutron in the nucleus is transformed into a proton and the emitted β -particle:



One of the isotopes of carbon, which occurs in very low abundance, is ${}^{14}_6\text{C}$ (spoken as carbon-14). When ${}^{14}_6\text{C}$ decays, it emits a β -particle.

What is the other product of ${}^{14}_6\text{C}$ decay?



Remember that the mass remains unchanged, but that the atomic number of the nucleus *as a whole* increases by one. The product therefore has atomic number 7, and from the Table in Appendix 1 you can see that it is nitrogen:



4.1.3 γ -Radiation

γ -Radiation is electromagnetic radiation (photons) of very short wavelength (high energy), usually much shorter even than those of X-rays (Unit 9). Since photons have neither charge nor mass, emission of a photon of γ -radiation does not change the mass number or atomic number of a nucleus. γ -Ray emission, in fact, often accompanies radioactive decay processes.

γ -radiation

4.2 Radioactive decay

When radioactive carbon, $^{14}_6\text{C}$, decays as shown in equation 7, it is converted to the most stable isotope of nitrogen. You might expect that the total amount of $^{14}_6\text{C}$ on the Earth was therefore continually being reduced. In fact, the total amount stays remarkably constant because $^{14}_6\text{C}$ is also constantly being *produced* in the upper atmosphere by bombardment of nitrogen by cosmic rays. As a result, the carbon in the atmosphere, present as carbon dioxide, has a constant fraction of $^{14}_6\text{C}$ in it. When a plant converts this carbon into living tissue, the $^{14}_6\text{C}$ fraction of the tissue is the same as that of the atmosphere, and it remains the same as long as the tissue is living and exchanging its carbon with the atmosphere. Only when the plant dies does the amount of $^{14}_6\text{C}$ in the plant begin to decrease by decaying to $^{14}_7\text{N}$, because it is then no longer absorbing carbon dioxide.

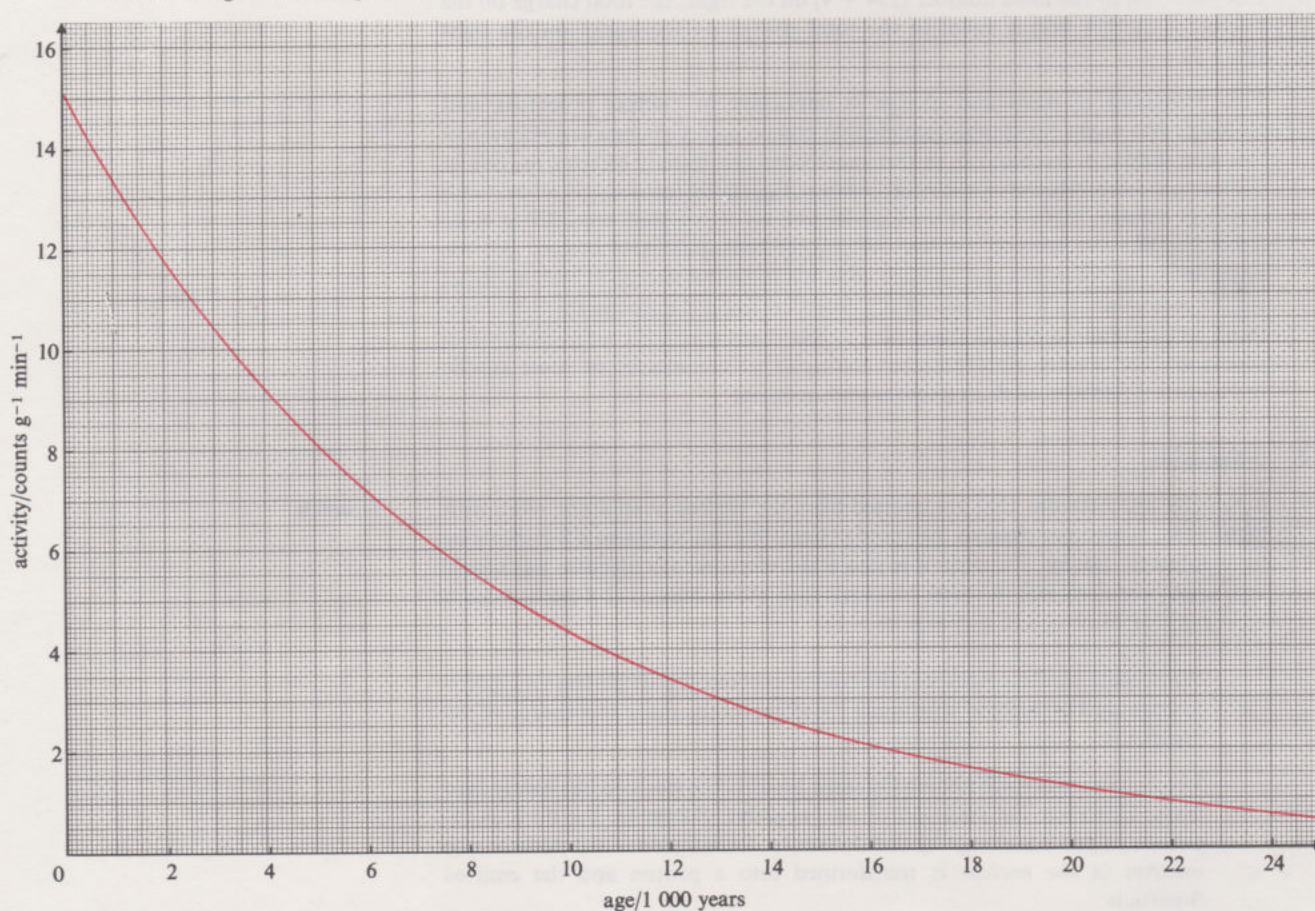


FIGURE 13 Radioactive decay curve of $^{14}_6\text{C}$. One count is equivalent to one β -emission. Now a particularly important feature of the decay of a radioactive element is the rate at which the decay occurs. Some nuclei decay very fast and others very slowly. Figure 13 shows how a sample of $^{14}_6\text{C}$ decays from its 'natural' activity level of about 15 β -emissions per minute per gram of carbon (all isotopes of carbon present).

Mark on the curve the time for the activity to reduce to half of its original value, and also for the remainder to decay to half of its activity (that is, a quarter of the original value). What do you notice about the two times?

Both time intervals are equal, about 5 700 years. You could extend this to $\frac{1}{8}$, $\frac{1}{16}$ and so on; in each case the interval would be the same. We can generalize this result: the time taken for half of a radioactive sample to decay is constant. We call this time the *half-life*. Rather surprisingly, the rate of decay, and hence the

half-life

half-life of an isotope, is totally independent of the chemical environment of the isotope or of the temperature. It makes no difference whether the ^{14}C exists as carbon or is combined with oxygen in the gas carbon dioxide.

An important use of ^{14}C may have occurred to you. Can you think what this is?

If ^{14}C decays at a known rate (Figure 13) after a plant dies, the present amount of ^{14}C in the dead plant tells us when it died. ^{14}C can be used as a 'clock' for the time-scale covering tens of thousands of years. This is the time-scale of civilization, so ^{14}C is a means of dating archaeological specimens, and the method is called *carbon dating*.

A sample of linen covering the Dead Sea scrolls has an activity of 12.0 β -emissions per gram per minute. How old are the scrolls?

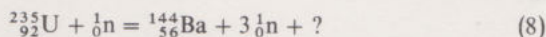
The age of the linen (estimated by reference to Figure 13) proves that the scrolls are about 2000 years old, and possibly older although not necessarily a contemporary record of the Book of Isaiah (about 500 BC).

^{14}C is just one of the many radioactive isotopes. Others, for example some of those in Table 3, have very long half-lives, on the time-scale of geological processes, which will be discussed in Unit 26.

4.3 Nuclear fission and nuclear fusion

The product of radioactive decay is an isotope with an atomic number close to that of the original isotope. However, in 1939 two German scientists, O. Hahn and F. Strassmann, discovered the element barium as a product of the radioactive isotope ^{235}U . Now barium has an atomic number of 56, and in the decomposition of ^{235}U , neutrons are also produced. In fact, they take part in the reaction.

What is the other product of this reaction?



Because the total mass number and charge are conserved in nuclear reactions, the atomic number of the product is

$$92 - 56 = 36$$

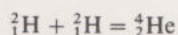
and the mass number is

$$(235 + 1) - (144 + 3) = 89$$

As you can tell from Appendix 1, element number 36 is krypton, so the product is $^{89}_{36}\text{Kr}$.

You can see that equation 8 represents a quite different process to a simple radioactive decay. When bombarded by neutrons, the $^{235}_{92}\text{U}$ nucleus splits into two smaller nuclei plus more neutrons. This splitting process is known as *nuclear fission*. The reaction shown in equation 8 occurs in a nuclear power station and in the first types of nuclear bomb. As you have read in Unit 8, vast quantities of energy are released in nuclear fission. You will probably have noticed too that the date of Hahn and Strassmann's discovery was just before the outbreak of the Second World War. The flurry of research into nuclear fission which followed, resulted in the U.S.A. being first to develop a power station and the 'bomb'.

Now, more than thirty years after the first nuclear bomb, it is the hydrogen bomb which is regarded as the ultimate weapon. Just as heavy nuclei break down to lighter ones, so very light nuclei can be made to fuse to form heavier ones. In the hydrogen bomb we are in fact simulating, on a relatively minute scale, the nuclear processes that occur in the Sun. For example, deuterium atoms, which are isotopes of hydrogen consisting of one proton and one neutron, combine to form helium atoms in a process called *nuclear fusion*:



carbon dating

TABLE 3
The half-lives of some isotopes

Isotope	Half-life
${}^3_1\text{H}$	12.26 years
${}^6_4\text{Be}$	4×10^{-21} seconds
${}^7_4\text{Be}$	53 days
${}^8_4\text{Be}$	2×10^{-16} seconds
${}^9_4\text{Be}$	stable*
${}^{10}_4\text{Be}$	2.5×10^6 years
${}^{11}_4\text{Be}$	13.6 seconds
${}^{10}_6\text{C}$	19 seconds
${}^{11}_6\text{C}$	20.3 minutes
${}^{12}_6\text{C}$	stable*
${}^{13}_6\text{C}$	stable*
${}^{14}_6\text{C}$	5730 years*
${}^{15}_6\text{C}$	2.4 seconds
${}^{16}_6\text{C}$	0.74 second
${}^{18}_9\text{F}$	1.83 hours
${}^{19}_9\text{F}$	stable*
${}^{22}_{11}\text{Na}$	2.60 years
${}^{23}_{11}\text{Na}$	stable*
${}^{32}_{15}\text{P}$	14.3 days
${}^{32}_{16}\text{S}$	stable*
${}^{35}_{16}\text{S}$	88 days
${}^{40}_{19}\text{K}$	1.28×10^9 years*
${}^{40}_{20}\text{Ca}$	stable*
${}^{87}_{37}\text{Rb}$	5.0×10^{11} years*
${}^{90}_{38}\text{Sr}$	28 years
${}^{137}_{55}\text{Cs}$	30 years
${}^{235}_{92}\text{U}$	7.1×10^8 years*
${}^{238}_{92}\text{U}$	4.51×10^9 years*

* Occurs naturally

nuclear fission

nuclear fusion

We examine the composition of the Sun and other stars in TV 11, and in Unit 30 we shall return to the topic of energy release in nuclear reactions. At the moment you should know as much about the nucleus of an atom as you need to understand the model of the atom that we shall develop in these Units.

4.4 Summary of Section 4

It is worth while at this stage to summarize the atomic model that we have developed so far.

1 Matter consists of atoms, which are very small (diameters typically about 3×10^{-10} m).

2 The mass of an atom, for example of neon, is about 10^{-26} kg. However, elements contain atoms of different masses. These are called isotopes.

3 The α -particle scattering experiment shows that the mass and positive charge of the atom is concentrated at the nucleus (typical diameter about 10^{-14} m). The vast empty space around the nucleus contains the negative charge, as electrons.

4 Elements are distinguished by the number of protons in the nucleus, the atomic number, Z . The mass number is the sum of the number of protons and neutrons in the nucleus.

5 The range of elements is limited to about 100, the heavier ones often being unstable. They decompose by emitting α - or β -particles or by nuclear fission.

As this brief summary shows, our picture of an atom has developed far beyond the fuzzy dots shown in Figure 1. But it is also far from complete. With the information you have gained so far, you should be able to do the following things:

Show that you have some idea of what is meant by the terms: 'nuclear reaction', 'radioactivity', ' β -particle', ' γ -radiation', 'radioactive decay', 'half-life', 'carbon dating', 'nuclear fission', 'nuclear fusion'.

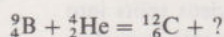
Complete balanced equations depicting nuclear reactions. Give examples of important nuclear reactions as outlined in Section 4.

Determine the age of a sample containing carbon, given its activity and Figure 13.

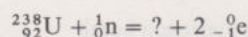
To test your achievement of these Objectives, try the following SAQs.

SAQ 13 A sample of cedar wood taken from the Egyptian pyramid at Snefuru has an activity of 8.3 β -emissions per gram of carbon per minute. How old is the sample?

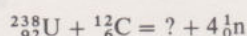
SAQ 14 In 1932 in a series of experiments with α -particles, Chadwick bombarded atoms of boron (symbol B) with α -particles and produced carbon-12. What was the other product?



SAQ 15 In a nuclear reactor, ${}^{235}_{92}\text{U}$ undergoes fission and releases free neutrons. If another isotope of uranium, ${}^{238}_{92}\text{U}$, is present, it captures a neutron, but subsequently emits two β -particles (electrons, ${}^0_{-1}\text{e}$). What is the atomic number of the product? Remember that the β -particle has nearly zero mass and a charge of -1 .



SAQ 16 The nuclear reaction described in SAQ 15 has been exploited in making several new heavy elements. What is the atomic number of the element produced in the following process, in which ${}^{238}_{92}\text{U}$ is bombarded with carbon nuclei, ${}^{12}_6\text{C}$?



With the broad picture of the atom described in the summary, we shall now proceed to examine in a little more detail the arrangement of electrons in atoms. If you are wondering where this exploration of atomic structure is leading, please be patient. In Unit 13 you will encounter one of the most important scientific relationships to be discovered in the past century: the relationship between chemical behaviour and atomic structure. Consider the three elements fluorine, neon and sodium. Their atomic numbers are 9, 10 and 11, respectively (see Appendix 1). This implies that their nuclear charges are 9, 10 and 11, respectively, and that their atoms contain 9, 10 and 11 electrons, respectively. So what effects do these numbers have on their chemical properties?

Fluorine is a gas which reacts with almost all substances, usually vigorously. Neon is also a gas, but has not been found to react with any substance. Sodium is a metal, and reacts violently with water and air. In Unit 13 you will discover that the arrangement of electrons in these three very dissimilar elements provides an explanation for these properties. Consequently, for the remainder of these two Units we shall explore the *electronic structure* of atoms. Just as we cannot 'see' atoms directly, neither can we 'see' the arrangements of electrons in atoms. However, radiation of various sorts interacts with the electrons in atoms, revealing information that allows us to construct a model of the electronic structure of atoms. To begin, we shall investigate how electromagnetic radiation, and particularly light, interacts with atoms.

electronic structure

5 Atomic spectra

Home Experiment 2 Spectra

This Section starts with some simple observations with the hand spectroscope in the Home Kit. You will also need the mercury vapour lamp*.

1 The white light spectrum Take the spectroscope and look through it at an ordinary light bulb. When you point the end with the fine slit in it towards the bulb, you should see a spectrum of colours resembling Spectrum A on the colour plate. Hold the spectroscope so that the colours range from red on your left to violet on your right, and slide the lens holder part of the spectroscope in and out until the spectrum has sharp upper and lower edges. It is now roughly in focus. The spectrum ranges continuously from red to violet (and beyond, although you cannot see outside this range). It is produced by the *emission* of radiation by the hot wire in the lamp, and is called a *continuous spectrum*. Light that gives a continuous spectrum like that in Spectrum A of the colour plate, containing all possible frequencies of visible radiation, is known as white light.

emission spectrum
continuous spectrum

2 The mercury vapour lamp spectrum Now examine the spectrum of the mercury vapour lamp, preferably in a darkened room†. At the first attempt you may see a number of broad coloured bands. You may need to slide the focusing lens in or out to sharpen the picture until the bands become lines. You will probably find that you cannot bring all the lines into focus at the same time. (The best position of the focusing lens for, say, a yellow line is different from that for a violet line.)

Sketch what you see, on the same scale as the white-light spectrum. This should be easy, because, as background to the mercury spectrum, you will also see a continuous white light spectrum from a phosphorescent substance which coats the mercury lamp.

* For this purpose, remove the bulbholder assembly from the moth trap supplied in the Home Experiment Kit, Part 1. Put the mercury vapour lamp in the bulbholder. Place the bulbholder assembly on a table or other flat surface, and connect to the mains via the isolating transformer. If the lamp does not operate, take out the mains plug before checking the equipment, using the checklist in the moth trap instructions in the *Home Experiment Kit Booklet, Part 1*.

† Do not leave the mercury vapour lamp switched on for longer than is necessary, since it may cause irritation to your eyes.

If you have access to sodium street lights (these are the yellow ones), to bluish-white street lights, or to any of the various red and blue advertising lights collectively (but wrongly) described as 'neon lights', view these with the spectroscope and draw a diagram of what you see. (The colour plate shows the spectra of these lights, so retain your sketches for comparison). Are you now able to suggest what source is used in the bluish-white street lights? (See p. 74 for confirmation.)

In all the spectra you have seen, except the white-light spectrum, you will have observed distinct bright lines. These bright lines result from atoms that acquired energy from an electric discharge in the lamps. As you will see in Unit 12, when you have had a chance to perform some flame tests, bright line spectra are also produced when atoms are heated directly in a flame. Since they arise from atoms, we call them *atomic spectra*, and because they consist of lines they are also called *line spectra*.

If you have had the opportunity to observe several different sources, you will have noticed that each source gives rise to its own characteristic coloured line, or set of lines. The pattern is characteristic of the element producing the spectrum.

What use does this suggest for atomic spectroscopy?

Atomic line spectra, being characteristic of the elements that produce them, provide a means of analytical identification of elements. You will make some use of this in Unit 12 and we shall examine it again in this Unit.

3 The solar spectrum Sunlight enables us to see objects of all colours. You might, therefore, reasonably conclude that sunlight is genuinely white light, as in Spectrum A. Take your spectroscope and mount it on a piece of card as shown in Figure 14. This will shield your eyes from any direct view of the Sun. Now focus your spectroscope on any lines that you can observe when you point the spectroscope close to the Sun. The dark lines you should be able to see are called *Fraunhofer lines* after their discovery by J. Fraunhofer in 1814.

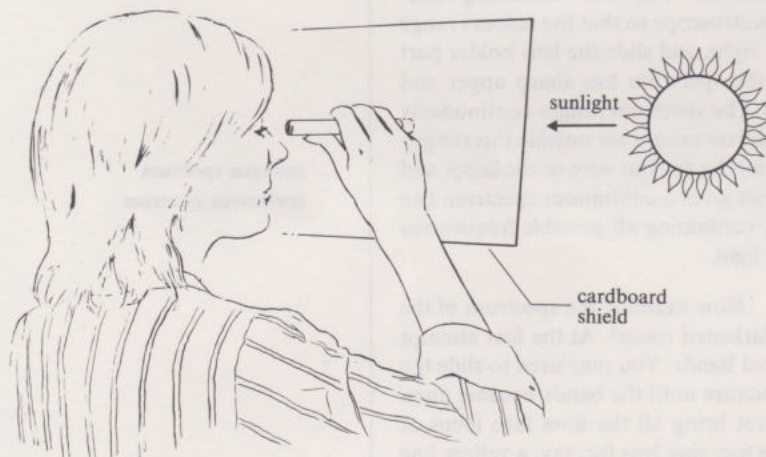


FIGURE 14 Using the hand spectroscope to observe the Sun's spectrum.

If the bright lines you observed in the mercury spectrum are *emission* lines, what would you call the dark lines in the Sun's spectrum?

Dark lines must result from the removal or *absorption* of light of certain frequencies from the white light emitted by the hot part of the Sun. Atoms in the Sun's atmosphere absorb particular frequencies, leaving gaps in the continuous spectrum (Figure 15). It may not surprise you to learn that the frequencies an atom selects for absorption are identical to those that the same atom emits when heated. We have already indicated that these frequencies are characteristic of the particular atom involved. (This point is illustrated in TV 11 and its significance will be discussed in more detail in a later Section of the Units.)

atomic spectra
line spectra

solar spectrum

Fraunhofer lines

absorption spectrum

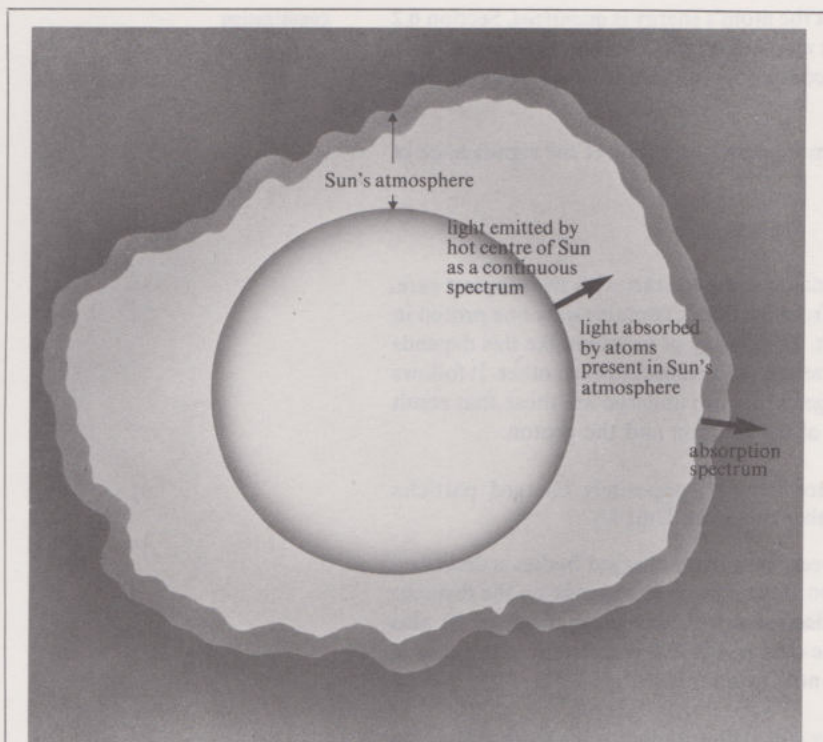


FIGURE 15 How the Fraunhofer lines are produced.

Now sketch the position of the Fraunhofer lines on the same scale as the white-light spectrum in Spectrum A. Compare the Fraunhofer absorption spectrum with the various atomic emission spectra illustrated on the colour plate, and suggest whether any of these atoms may be present in significant quantity in the Sun.

We follow up this exercise and extend it to stars in TV 11.

Obviously, atomic spectroscopy has fascinating and far-reaching applications. It is remarkable that, with such a simple piece of equipment, we can begin to analyse the Sun at a distance of about 1.5×10^{11} m!). But for our present purposes, we are more concerned with probing the structure of the atom (about 3×10^{-10} m in diameter) with the same technique.

5.1 The significance of line spectra

The line spectra you have examined with your spectroscope are not only beautiful; they are highly significant. They are direct evidence for a phenomenon that is quite outside our normal experience. Everything in our experience conditions us to think of energy as being continuously variable. As we cycle downhill, the bicycle moves smoothly faster and faster as it smoothly acquires kinetic energy; a billiard ball, once struck by a cue, slowly loses its kinetic energy until eventually it stops; a firework rocket shot in the air smoothly acquires gravitational energy as it goes up and smoothly loses it as it comes down. There are no restrictions on the energy changes possible in any of these systems. It was the cause of some consternation, therefore, when it was suggested at the end of the last century that atoms are restricted in the way they can change their energy.

As we shall demonstrate in succeeding Sections, line spectra show that an atom can only change its energy by certain fixed amounts. The energy possibilities for an atom are *not* continuously variable as they are, for example, for the ball on a billiard table. You know that when a stationary billiard ball is hit by another ball, the two exchange energy whatever the energy of the moving ball. If the stationary ball were to behave like an atom, it would be choosy about the magnitude of the energy which it would exchange. It could adopt only 'permitted' energies, and would be unable to interact with bodies that did not supply this exact energy.

We describe the situation by saying that the atom's energy is *quantized*. Section 6.2 of Unit 9 makes the point that light is also quantized. When light interacts with matter, it is best described not as a continuous wave but as a stream of little packets of energy called photons.

Let us look at a simple spectrum in more detail to interpret the significance of these quantized energy changes.

5.1.1 The spectrum of atomic hydrogen

If we wish to interpret line spectra, it makes sense to start with the simplest case. The hydrogen atom, as you will recall from Section 3, contains only one proton in the nucleus and one electron outside it. The energy of a system like this depends on how the electron and proton are arranged with respect to each other. It follows that the only energy changes the hydrogen atom can undergo are those that result from changes in the relative positions of the electron and the proton.

What does the electrostatic force between oppositely charged particles depend on? (You should remember this from Unit 8.)

The electrostatic attraction between oppositely charged bodies is described by Coulomb's law (Unit 8, Section 10.2). The force depends on the distance between the charged bodies; it decreases with increasing distance. (It also depends on the magnitude of the charge, but this is constant in the case of the hydrogen atom, so we need not consider it.)

In the hydrogen atom (as, indeed, in any atom) there is an attractive force between the electron and the positively charged nucleus. If the electron is to move away from the nucleus, energy will have to be supplied to overcome this attractive force. If the electron now moves back to its original position, exactly the same amount of energy will be released as was supplied in the first step. (This follows from the principle of the conservation of energy, which you met in Unit 8.)

One of the ways in which release of energy can manifest itself is emission of electromagnetic radiation. Similarly, absorption of electromagnetic radiation means that energy is being absorbed.

With this in mind, let us now look at the emission spectrum of the hydrogen atom. The visible part of the spectrum consists of just four sharp lines. (Spectrum B on the colour plate.)

What does Spectrum B tell you about the energy changes possible for the hydrogen atom?

(i) In comparison with Spectrum A, the continuous spectrum, Spectrum B, contains a very limited number of frequencies. Only four visible frequencies appear, whereas in the continuous spectrum all possible frequencies are represented.

A limited number of emission frequencies testifies to a limited number of energy changes of the electron in the atom. You should remember from Section 6.2 of Unit 9 how energy and frequency are related by the equation

$$E = hf$$

where h is Planck's constant $= 6.626 \times 10^{-34} \text{ J s}$,

f is expressed in hertz (s^{-1}),

and E in joules.

(ii) The sharpness of the lines shows that the energy jumps are very specific in size.

It would be nice to know if the spectrum continues beyond the range our eyes can see. Luckily, photographic film has a wider range of sensitivity than the human eye and can 'see' both into the ultraviolet and infrared. If, instead of just looking down the spectroscope, we take a photograph of the spectrum, we can see that the pattern of emission lines continues into the ultraviolet: Figure 16 indicates the spectrum that can be obtained in such a photograph.

You will notice that the series continues into the ultraviolet, but not the infrared. This series of lines, which was first studied by the physicist J. J. Balmer in the late

nineteenth century, is called the Balmer series. You can hear more about the significance of his work in Radio 05, and you will have an opportunity to study this spectrum yourself at Summer School.

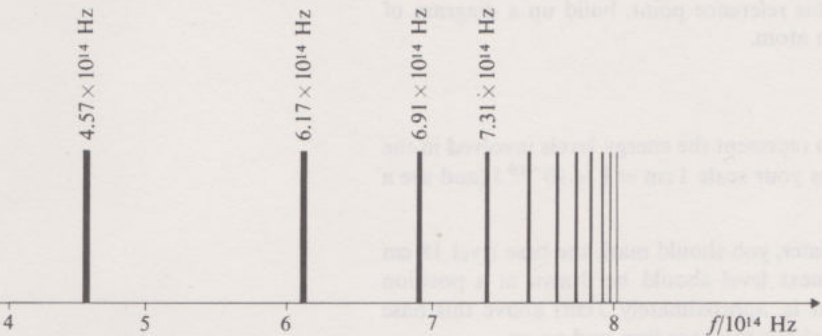


FIGURE 16 The Balmer series in the atomic spectrum of hydrogen. This emission spectrum and all subsequent spectra in these Units are depicted as black lines on a white background. In practice, photographs of emission spectra appear as white lines on a black background.

What do you notice about the spacing of the lines in this series?

They get closer together at higher energy. (We shall return to this observation in Section 5.4.)

Table 4 lists the frequencies at which the first seven lines of the spectrum in Figure 16 are observed. We have also listed the corresponding photon energies.

You should now be able to relate atomic spectra to energy changes.

You can test your achievement of this Objective with SAQ 17.

SAQ 17 Use Spectrum B to make an estimate of the energy change corresponding to the red emission line in the spectrum of the hydrogen atom.

If you had any trouble with SAQ 17, make sure you follow the working of this calculation for the blue line (given below Table 4).

TABLE 4
Frequencies and energy changes for the lines in the Balmer series of hydrogen

Line	Colour	Frequency/ 10^{14} Hz (or s^{-1})	Energy change/ 10^{-19} J
1	red	4.57	
2	blue	6.17	4.09
3	violet	6.91	4.58
4	dark violet	7.31	4.84
5	ultraviolet	7.55	5.00
6	ultraviolet	7.71	5.10
7	ultraviolet	7.81	5.18

blue line: $E = hf$, where h is Planck's constant

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$f = 6.17 \times 10^{14} \text{ Hz (or } s^{-1})$$

$$E = 6.626 \times 10^{-34} \text{ Js} \times 6.17 \times 10^{14} s^{-1}$$

$$= 4.09 \times 10^{-19} \text{ J}$$

5.2 The energy-level diagram

The simple pattern in Figure 16 invites a simple explanation. You already know that the energy changes permitted to an electron in the hydrogen atom are sharply defined, and that each line in the emission spectrum is the result of an electron 'jump' from higher to lower energy. This strongly suggests that the electron energies in the atom are themselves sharply defined. We can represent the electron energies on a diagram as *energy levels*.

electron energy level

If we assume that all the electron jumps responsible for the spectral lines in Figure 16 terminate in the same lower level, the spectrum is easily interpreted. We can take this level as a base-line and arbitrarily give it zero energy, and then, by measuring each of the jumps from this reference point, build up a diagram of electron energy levels in the hydrogen atom.

Exercise 1

On Figure 17, draw horizontal lines to represent the energy levels involved in the spectrum shown in Figure 16. Take as your scale $1\text{ cm} = 1 \times 10^{-19}\text{ J}$ (and use a sharp pencil!).

For reasons that will become clearer later, you should mark the base level 18 cm from the bottom of the page. The next level should be drawn at a position corresponding to $3.03 \times 10^{-19}\text{ J}$ (that is, approximately 3 cm) above this base level, then another at $4.09 \times 10^{-19}\text{ J}$ above the base-line, and so on.

This diagram is called an *electron energy-level diagram*.

energy-level diagram

It is now an easy matter to represent on your diagram the electron jumps producing the emission spectrum of Figure 16. From each level in the diagram draw a downward-pointing arrow terminating at the base level. This indicates the loss in energy when the electron jumps to this level from a higher one. (Try not to fill up more than the left-hand third of the page with arrows at this stage: you will be using the rest of the diagram in later Sections.)

SAQ 18 What is the energy of the photon emitted when the electron jumps between the highest level of Figure 17 and the second lowest?

5.3 The Lyman series

It is not surprising that the first series of spectral lines observed for the hydrogen atom lay at least partly in the visible region of the electromagnetic spectrum. The visible lines cannot fail to be noticed by anyone who investigates the spectrum of atomic hydrogen. But before we conclude that an electron energy-level diagram based on this series offers a complete description of the hydrogen atom's electronic energies, it would be wise to look in other spectral regions for other possible series.

If the hydrogen atom has more energy levels, apart from those shown in Figure 17, in which spectral region would you expect to find evidence for this?

The spectral lines in Figure 16 are getting closer and closer together with increasing frequency, suggesting that the higher electron energy levels also converge. To fit in extra levels at energies far higher than all the others would break the pattern of converging lines. But it would be quite possible to imagine other *low* energy levels. If there are energy levels below the lowest one drawn on Figure 17, we would expect transitions that terminate on the new level(s) to lie in the ultraviolet.

Why?

Because the energy differences between higher energy levels and any new, low one are larger than any shown so far on Figure 17, the frequencies of corresponding spectral lines must be higher than those in the visible range.

In fact, investigation of the ultraviolet region shows that there is another series of lines in the hydrogen spectrum, which lies in the region $2 \times 10^{15}\text{ Hz}$ to $3.5 \times 10^{15}\text{ Hz}$. These lines are produced by transitions to a level that lies $16.34 \times 10^{-19}\text{ J}$ below the lowest level you have previously drawn in Figure 17. (You should now include this line on your energy-level diagram.) A survey of the far ultraviolet and X-ray regions fails to reveal any other series of lines due to atomic hydrogen, so the level you have just drawn in Figure 17 is, in fact, the *lowest* energy level in the hydrogen atom. Now that you have a complete picture of the energy levels in the hydrogen atom, it is useful to be able to refer to them. Label the lowest level 1. Succeeding energy levels can then be numbered, for convenience, 2, 3, 4, etc. The number given to any particular 'level' is known as its *principal quantum number*, given the symbol ' n ', where n can equal 1, 2, 3, 4, ... etc.

principal quantum number, n

In a hydrogen atom the single electron is usually to be found in the lowest possible level ($n = 1$). This corresponds to the *ground state* of the atom. The

ground state

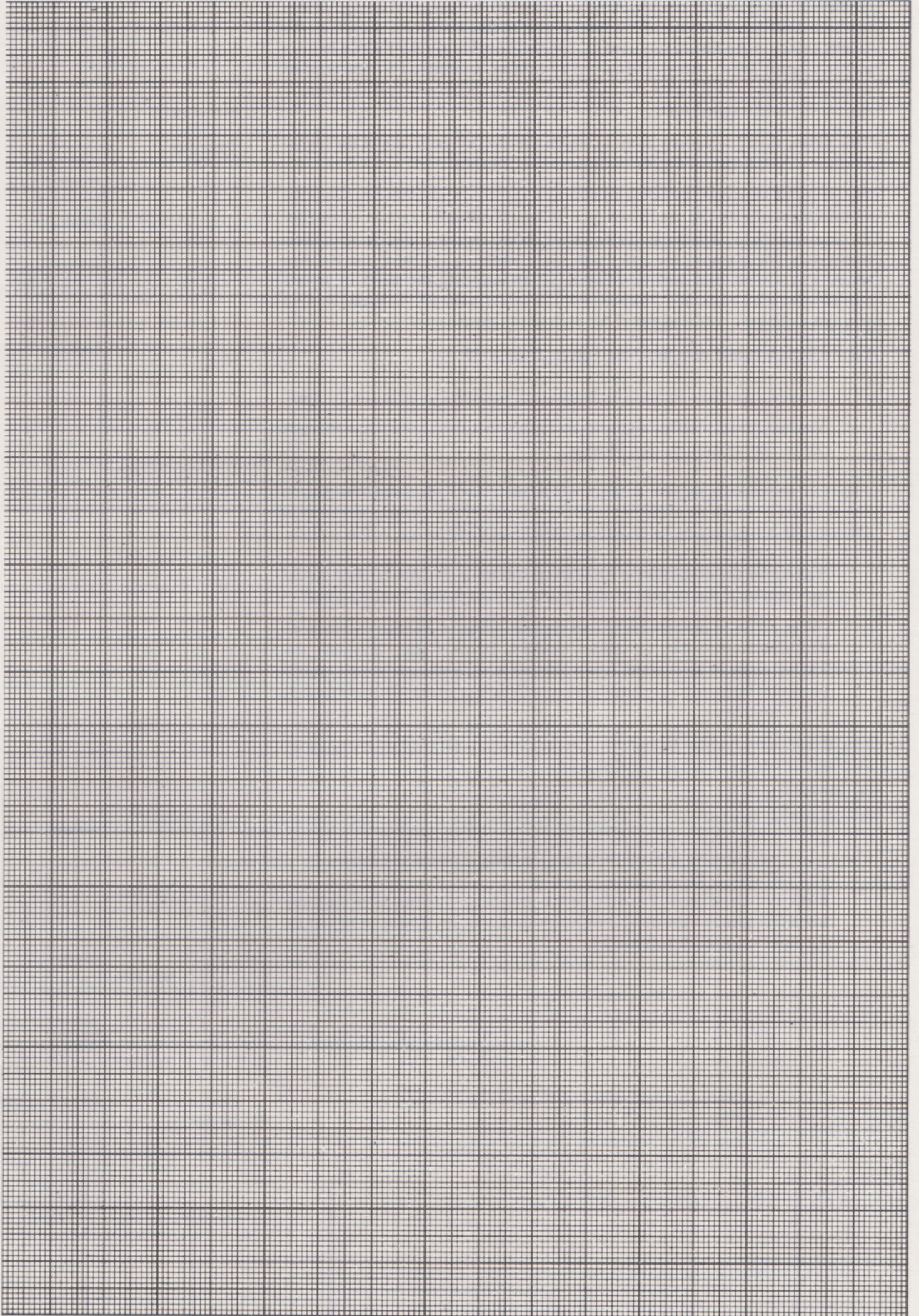


FIGURE 17 Your energy-level diagram for hydrogen.

electron can only occupy one of the higher energy levels if the extra energy for this has been obtained from some other source. This source could be a photon, or the kinetic energy of the electrons or ions in an electric discharge (like the one in your mercury lamp). When energy is absorbed by an atom, an electron is transferred to an electron energy level higher than the lowest level, and we say that the atom is *excited* or 'in an excited state'.

This means that a hydrogen atom in which the electron is in any of the higher levels, $n = 2, 3, 4$, etc., of Figure 17, is in an excited state.

The series of lines corresponding to electron jumps or 'transitions' between the various higher levels and the lowest ($n = 1$) level is called the Lyman series after its discovery by T. Lyman in 1906. Other series are also named after their discoverers; for example, the series with lower level $n = 3$ is called the Paschen series. You should now complete Figure 17 by including the series of arrows representing the Lyman and Paschen series. It would make the diagram clearer if you use a different coloured pencil for each of the three series.

Your diagram should now look like Figure 21 on p. 39.

Do you expect any series of hydrogen emission lines to lie in the infrared?

Yes: any series terminating in levels higher than $n = 2$ will have energies lower than that of visible radiation.

Figure 18 shows the complete emission spectrum of the hydrogen atom. As you can see from a close look at Figure 18, there is some overlap between the series in the infrared corresponding to transitions terminating at $n = 3, n = 4, n = 5$, etc.

Remember the discussion of absorption spectra in Section 5. How would you represent the process of absorption on your energy-level diagram?

When an atom absorbs energy, an electron jumps to a higher energy level. This is represented by an upward-pointing arrow. Figure 19 shows the Lyman series in absorption. It is produced when hydrogen atoms absorb particular frequencies from continuous radiation in the far ultraviolet region of the spectrum.

You should now be able to represent or interpret on an electron energy-level diagram the energy jumps corresponding to:

- emission spectra;
- absorption spectra.

Check your understanding of these Objectives by doing the following SAQ.

SAQ 19 Use Figure 17 and Table 4 to predict the frequencies of the three lowest-frequency absorption lines in the Lyman series. Which energy levels are involved in each transition?

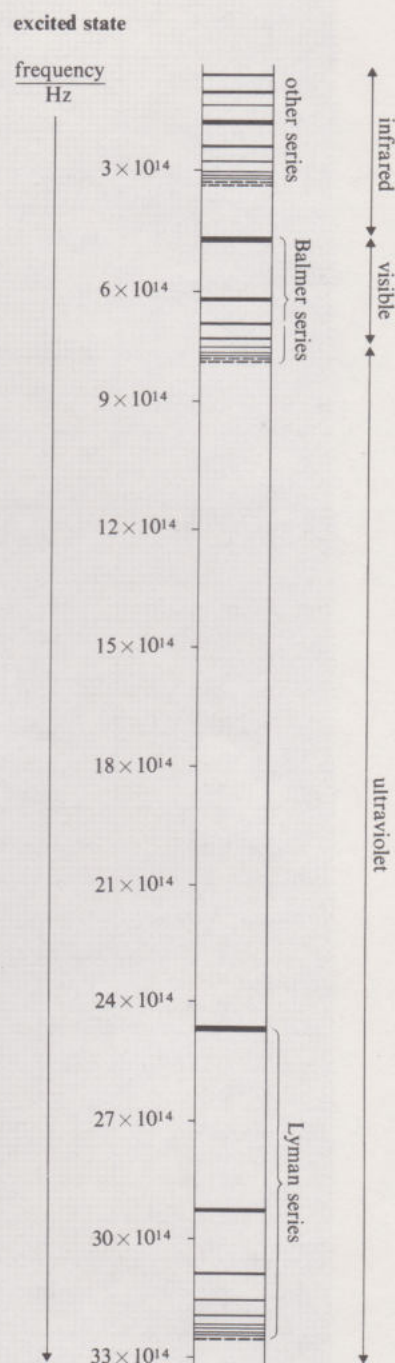


FIGURE 18 Complete atomic spectrum of hydrogen.

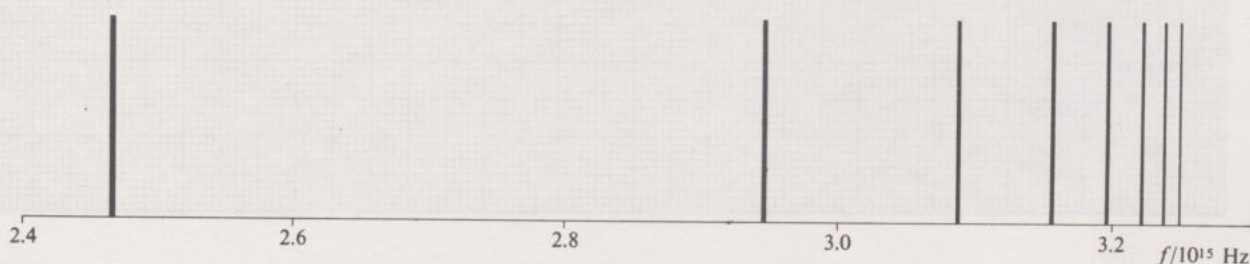


FIGURE 19 The Lyman series as an absorption spectrum of hydrogen.

5.4 Ionization energy

Your electron energy-level diagram (Figure 17) summarizes our knowledge of the behaviour of the electron in the hydrogen atom.

1 It emphasizes the fact that the electron in the atom can only have certain energies characterized by whole numbers, called quantum numbers. We say that the electron energies are 'quantized'.

2 It indicates the values of these allowed energies relative to the lowest level (with principal quantum number $n = 1$), which is arbitrarily given $E = 0$.

3 It shows how the electron can jump between allowed levels, absorbing or emitting photons of electromagnetic radiation.

4 The energy of the photon emitted or absorbed is, of course, equal to the energy difference between the levels concerned.

One other property of the diagram will have forced itself to your attention (particularly if your pencil was blunt!) The energy levels get closer together at higher energy. Eventually, they become so close together that it is impossible to tell one level from the next; they merge into a continuous band. We call this the *continuum*, and the energy at which it starts the *continuum level*.

continuum
continuum level

We can illustrate the situation graphically by plotting E_n , the energy of the level labelled n (measured from the $n = 1$ level; assuming $E_1 = 0$) against the principal quantum number, n .

Exercise 2

On Figure 20, plot energy E_n against principal quantum number n , using a scale $1 \text{ cm} = 1 \times 10^{-19} \text{ J}$.

The first two points are shown. Complete the graph using data from Table 4. Remember to add $16.34 \times 10^{-19} \text{ J}$ to each of the energies in Table 4, because in this exercise you are assuming $E_1 = 0$. The points should lie on a smooth curve.

Extend the graph beyond $n = 9$ by continuing the line of the curve. (This process of extending a graph beyond the measured data is called *extrapolation*. You may find it easier to do this if you draw a smooth curve through the points. Remember, though, that only integral values of n have any physical significance.)

MAFS 3

Estimate a value of E_n for (i) $n = 10$

(ii) $n = 14$

It is evident from the shape of the curve that the energy is not likely to exceed a certain limiting value.

What does this mean?

There is an upper limit to the energy an electron can have in an atom. If the electron is given more energy than this limiting value, it escapes from the atom. The electron is no longer bound to the nucleus and its energy is no longer quantized. If an atom absorbs a photon with more energy than is needed to remove the electron from the atom, the excess takes the form of kinetic energy, that is, energy of motion of the electron away from the nucleus.

The minimum energy required to remove an electron from an atom originally in its ground state is known as its *ionization energy*, I . As you will see in later Units, ionization energy is a quantity of considerable importance in understanding atomic structure and in chemistry generally.

ionization energy, I

What is your estimate of the ionization energy of hydrogen from Figure 20?

Estimate the highest and lowest value of the ionization energy of hydrogen that you could obtain by extrapolating the data in Figure 20. Using these estimates, within what error limits are you confident that the true answer lies?

(Our estimate of the ionization energy of hydrogen and a diagram (Figure 51), illustrating the shape of the plot you should have obtained, are given on p. 74.)

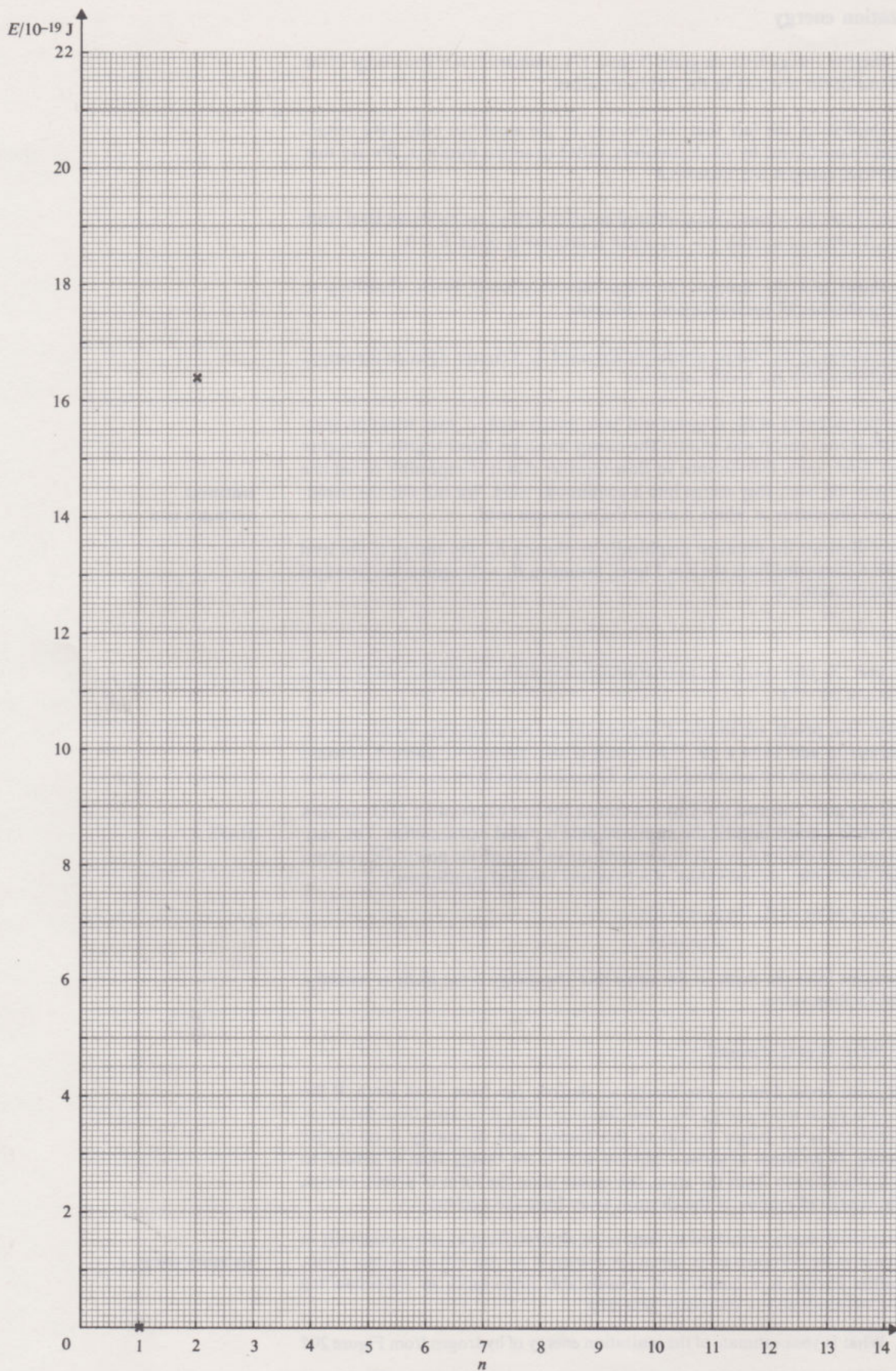


FIGURE 20 Your plot to estimate the ionization energy of hydrogen.

Now look at Figure 19, which shows the complete absorption spectrum of atomic hydrogen. Here you can see the dark absorption lines getting closer and closer. Eventually they will merge into a continuum. If we can estimate the frequency at which continuous absorption commences, we can easily find out how much energy is needed to remove an electron from the ground-state hydrogen atom.

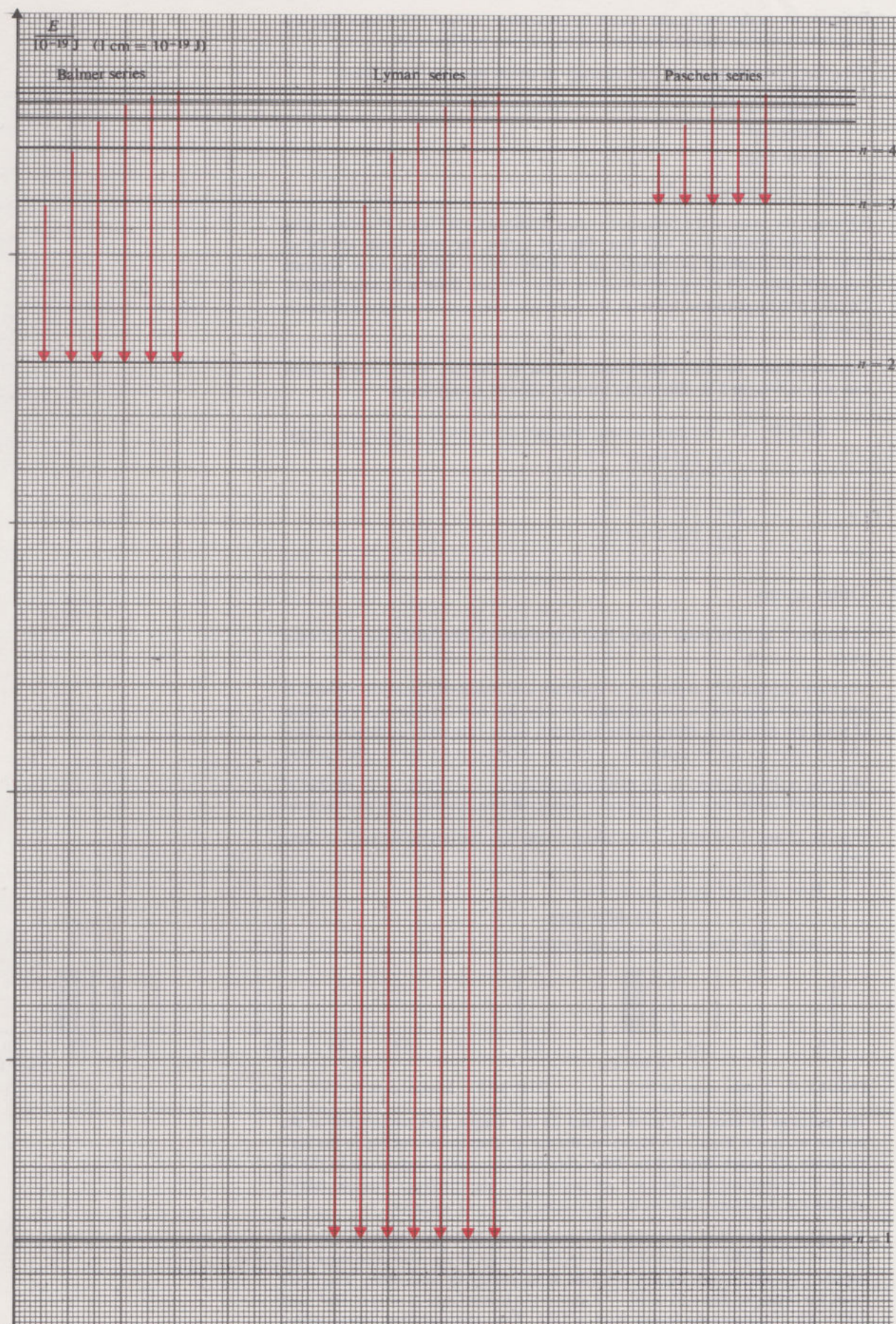


FIGURE 21 Energy levels for hydrogen and the transitions that produce three series.

Estimate where this continuum occurs by inspection of Figure 19. Check that this is in reasonable agreement with your extrapolation in Figure 20.

Enter here your estimate of the frequency at which the continuum starts.

Frequency, f , =

Energy, hf , =

Error limits \pm

Our answer is given on p. 74.

Although the value of the ionization energy obtained from Figure 19 should agree within experimental error with that obtained earlier, the error limits are rather large. Other graphical procedures are available which will give more accurate values of ionization energy from spectra. You will meet these at Summer School. For our present purposes, however, the value you have just obtained is sufficiently accurate.

You should now be able to appreciate that energy changes of electrons in *atoms* can only correspond to differences between allowed energy levels.

SAQ 20 Can the ground-state hydrogen atom absorb a photon of energy:

- (i) $21.34 \times 10^{-19} \text{ J}$
- (ii) $22.74 \times 10^{-19} \text{ J}$
- (iii) $17.5 \times 10^{-19} \text{ J}$
- (iv) $11.0 \times 10^{-19} \text{ J}$

5.5 Other atoms

In Section 5 we have come quite a long way towards understanding the hydrogen atom.

We have satisfactorily explained its spectrum and obtained some very significant quantitative information, the ionization energy. But how far does our knowledge of what the electron is doing in the hydrogen atom help us to understand other atoms? How far can we extend the treatment of Sections 5.1–5.4 to other atoms?

Without making matters much more complicated, we can look at the spectra of atoms such as the ions He^+ and Li^{2+} , which, like H, contain only one electron.

Figures 22 and 23 illustrate the highest-energy spectral series for each of these ions.

How do these spectra (a) resemble
(b) differ from
the Lyman series of the hydrogen atom?

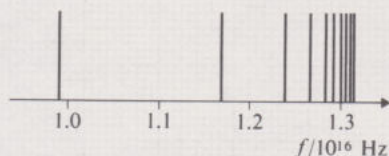


FIGURE 22 Lyman series for He^+ .

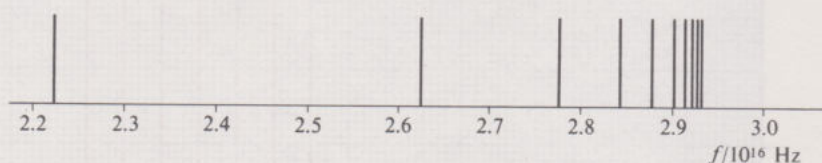


FIGURE 23 Lyman series for Li^{2+} .

The patterns of lines in Figures 22 and 23 are simple, and reminiscent of the pattern we saw in Figure 19. However, the energy changes giving rise to the He^+ spectrum are much larger than those obtained for similar transitions in the H atom. Transition energies for Li^{2+} are larger again, the spectrum obtained falling around the boundary between far ultraviolet and X-ray radiation.

The spectra show that He^+ and Li^{2+} are like the hydrogen atom in that the electron can only be accommodated in specific energy levels. They also show that similarly labelled levels do not have the same energy in each atom. The $n = 2$ level, for example, lies $6.54 \times 10^{-18} \text{ J}$ above the lowest level ($n = 1$) in He^+ , and $1.47 \times 10^{-17} \text{ J}$ above the lowest level in Li^{2+} . The corresponding energy difference for H is $1.634 \times 10^{-18} \text{ J}$.

When an atom has more than one electron, you may expect the situation to become more complex. Even if we restrict ourselves to energy jumps of one particular electron, it becomes necessary to consider interaction of this electron

with other electrons as well as the simple electron–nucleus interaction, which describes one-electron atoms. A consequence of this is that we get many more electron energy levels and it rapidly becomes increasingly difficult to disentangle the various overlapping series of lines that result.

However, a glance at Figure 24 (Na) and Spectrum D (He) on the colour plate shows that regularities are apparent in at least certain parts of the spectra of many-electron atoms.

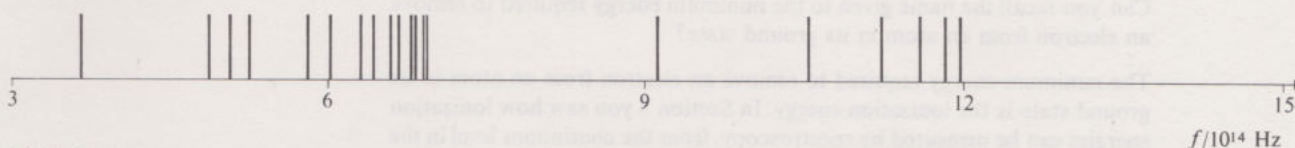


FIGURE 24 Part of the spectrum of sodium.

On the other hand, some spectra (Spectra J and L on the colour plate) are so highly complex that their interpretation is a major task even for the specialist.

5.6 Summary of Section 5

Again we can summarize the model of the atom that we have developed from our study of atomic spectra in Section 5.

The nuclear model of the atom envisages a small but massive nucleus consisting of protons and neutrons. The positive charge of the nucleus is balanced by the negative charge of the electrons, which occupy the relatively vast regions of space around nuclei.

Atoms absorb and emit radiation of certain 'permitted' frequencies which are characteristic of each type of atom. Since the energy of an atom can only change by the energies of the photons that the atom absorbs or emits, we infer that atoms can only have certain 'permitted' energies. The transitions between the permitted energies of the hydrogen atom are interpreted as jumps of the electron between different allowed electron energy levels, which are labelled with the principal quantum number, n ; n has integral values beginning with $n = 1$ for the lowest level.

At ordinary room temperatures the electron in hydrogen occupies the lowest level and the atom is in the ground state. The electron energy levels get closer together at higher energy and eventually merge to form a continuous band of energies, the continuum. An electron excited into the continuum is no longer bound by the atom; the atom is ionized.

Atoms with more than one electron produce more complex spectra with overlapping series of lines, although for some atoms, series can be recognized in the spectra.

Now that you have completed Section 5, you should be able to do the following things:

Show that you have some idea of what is meant by the terms: 'emission spectrum', 'continuous spectrum (white light)', 'atomic spectra', 'line spectra', 'absorption spectrum', 'solar spectrum', 'quantization', 'energy-level diagram', 'electron energy level', 'principal quantum number, n ', 'ground state', 'excited state', 'ionization energy, I ', 'continuum', 'continuum level'.

Outline a model of an atom, which is consistent with the information provided by its emission or absorption spectrum. You will see in the next Section how this model is adapted to include the information provided by another kind of spectrum—the photoelectron spectrum.

To test your achievement of these Objectives, try the following SAQs.

SAQ 21 What is the energy of the $n = 1 \rightarrow n = 7$ transition for (i) H, (ii) He^+ , (iii) Li^{2+} ?

SAQ 22 Can you suggest a reason why the electron in He^+ should be more tightly held than that in H, and the Li^{2+} electron should be more strongly held than that in He^+ ?

6 Shells, sub-shells and the second quantum number

Fortunately, we can obtain a great deal of information about the arrangement of electrons in an atom by measuring the energy required to *remove* electrons from atoms.

Can you recall the name given to the minimum energy required to remove an electron from an atom in its ground state?

The minimum energy required to remove an electron from an atom in its ground state is the ionization energy. In Section 5 you saw how ionization energies can be measured by spectroscopy, from the continuum level in the electron energy-level diagram.

Consider an atom of sodium. Its atomic number is 11, so there are 11 electrons in the atom. Suppose that we could remove all these electrons one at a time.

Would you expect the energies required to remove each of these 11 electrons in turn to be the same? What is the reason for your answer?

After one electron is removed, the atom consists of 10 electrons and a nucleus with 11 positive charges. The atom now carries a net positive charge. It follows that the second electron will be more difficult to remove than the first because the negatively charged electron is held more strongly by the atom. You might expect that the energy needed to remove successive electrons would increase, perhaps in some regular way. These energies are called *successive ionization energies**. Table 5 lists the successive ionization energies for sodium.

A plot of these values reveals a pattern more clearly than the Table does. Figure 25 shows that each successive electron requires more energy to remove it.

successive ionization energies

TABLE 5 Successive ionization energies of sodium/ 10^{-19} J

1st	8.23
2nd	75.71
3rd	115.30
4th	158.37
5th	222.27
6th	275.76
7th	333.41
8th	423.01
9th	479.97
10th	2 340.80
11th	2 648

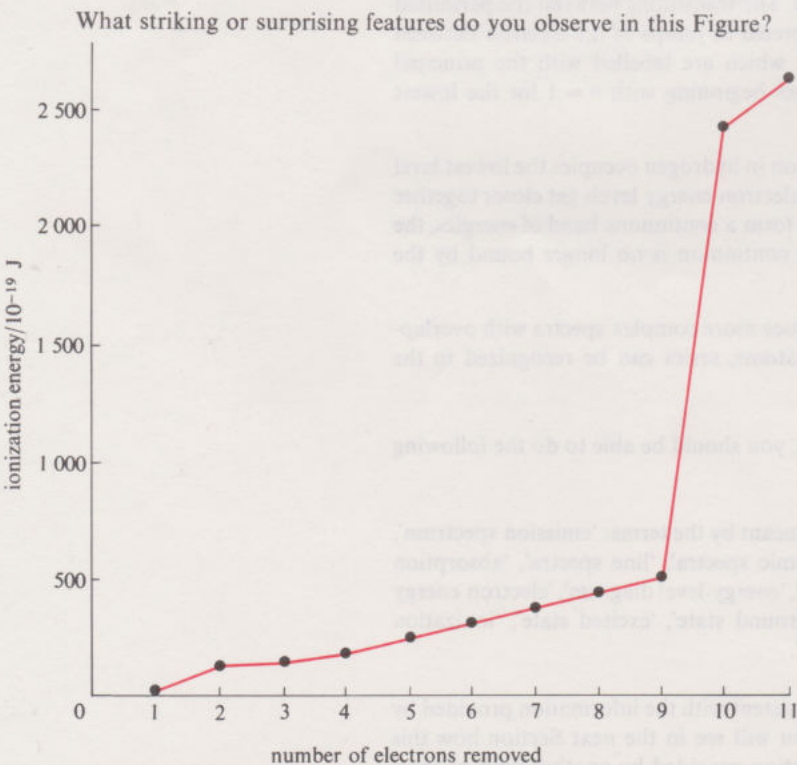


FIGURE 25 Successive ionization energies for sodium.

Firstly, it is obvious that the successive ionization energies do not increase in a regular way, although there appears to be a pattern in the values. Thus, the first

* Successive ionization energies can be measured by a technique you have encountered in a different context, mass spectrometry (discussed in TV 10). By steadily increasing the energy of the electron beam, the energy required to produce successively charged ions can be measured. Normally, these energies are measured in electron volts (eV), but for ease of comparison of energies, we have converted them to joules in Table 5. $1\text{ eV} = 1.602 \times 10^{-19}\text{ J}$.

electron is much more easily removed than subsequent ones. The energy needed to remove each of the next eight electrons increases gradually but not very regularly. The last two electrons are held very tightly in the atom. Apparently, the electrons in sodium fall into three groups. The first electron removed is in a different group from the next eight, and the last two electrons make the third group. How are we to interpret these groupings?

The most easily removed electron is held with the smallest force by the nucleus. Conversely, the last two electrons removed are the most firmly bound. You will recall that the Coulomb law describes the relationship between the force that attracts two oppositely charged bodies and the distance separating them. The law implies that the most loosely bound electron is relatively far from the nucleus. This is the outermost electron. Conversely, the two most tightly bound electrons are relatively close to the nucleus, the innermost electrons. As Figure 26 shows, we can imagine the electrons (which are represented by red spots) being contained in *shells* closer to or further from the nucleus.

In Figure 26 the electrons with the highest ionization energy (the most tightly bound) are shown at the bottom of the Figure. The placing of the most tightly bound electrons at the bottom of this sort of figure is conventional, and we shall adopt it throughout the rest of these Units. But notice that it inverts the groups of electrons which we recognized in Figure 25.

Figure 25 reveals an important property of electrons in atoms—a property that you have already deduced from the appearance of *line spectra* of atoms in Section 5.

Can you detect what this property is?

Ionization energies have specific values, indicating that the electrons in atoms can only have certain 'permitted' energies. Using the spectrum of hydrogen in Section 5, you were able to construct an electron energy-level diagram for hydrogen, which you labelled with the principal quantum number, n . If the electron shells are numbered, starting with 1 for the innermost shell as in Figure 26, then these numbers correspond to the same principal quantum numbers that you used for the energy levels in the hydrogen atom.

The successive ionization energies of atoms of other elements reveal the same type of shell structure of the electrons as in sodium. The first shell is found to contain, at most, two electrons and the second shell contains, at most, eight electrons. In this way the successive ionization energies provide a simple but approximate picture of the electron energy levels within atoms.

However, ionization energies are expected to increase as the charge on the ion increases (Coulomb's law). So the removal of successive electrons does not readily reveal whether each of the electrons within an electron shell is held with the same energy in the atom, nor why the first shell contains two electrons and the second shell up to eight electrons. It seems that we cannot easily refine the electron shell model depicted in Figure 26 using values of successive ionization energies.

Luckily, we are able to use the results of a new and rather simple type of spectroscopy—*photoelectron spectroscopy*—which provides direct information on energy levels by allowing us almost to 'see' energy levels in atoms.

In Section 5 you saw that when hydrogen atoms are irradiated with ultraviolet light they absorb light of certain frequencies corresponding to the differences between energy levels in the atom.

Look at Figure 17 on p. 35. What would you expect to happen when a hydrogen atom in its ground state absorbs light with photon energy $E = hf = 40 \times 10^{-19} \text{ J}$?

The ionization energy, I , of a hydrogen atom is less than this energy ($I = 21.74 \times 10^{-19} \text{ J}$). Remember that when an atom absorbs a photon with energy higher than the ionization energy of the atom, the atom is ionized: an electron is ejected from the atom. As you know from Unit 9, the electron emitted when a substance is irradiated with photons is called a *photoelectron*.

Where will the excess energy appear?

electron shell



FIGURE 26 Electron energy shells for sodium.

photoelectron spectroscopy

photoelectron

As the photon is absorbed, the photon energy is used to increase the separation of the electron and the nucleus. The excess energy will appear as kinetic energy of the electron and nucleus moving apart. Practically all of this excess energy will belong to the photoelectron because the nucleus, being much more massive than the electron, remains effectively stationary.

Write an expression for the kinetic energy, E_k , of the photoelectron, in terms of the photon energy and the ionization energy:

$$E_k = ?$$

The expression you have written should be familiar. As you know from Unit 9, in the photoelectron experiment, electrons are emitted when the frequency of the radiation is equal to or greater than some threshold frequency, that is, when the photon energy exceeds some critical value. According to the principle of the conservation of energy, the kinetic energy of the photoelectron is just the difference between the photon energy, hf , and this threshold energy, I :

$$E_k = hf - I \quad (9)$$

As you see from equation 9, photoionization from gaseous atoms is similar in principle to photoelectron emission from a solid metal. The same relationship applies to each process. Equation 9 also shows that if we know the photon energy, and if we can measure the kinetic energy of the electrons, we can determine the ionization energy of the atom. This relationship between ionization energy and the kinetic energy of the photoelectron is the basis of photoelectron spectroscopy. The relationship between the terms in the photoelectric equation is more apparent if it is represented diagrammatically as in Figure 27, which shows the ionization energy as the difference in energy between the continuum level and the electron level.

Fortunately, the results of photoelectron spectroscopy turn out to be much more useful than those from successive ionization energies, because in photoelectron spectroscopy we can measure the energy required to remove *each* electron from the *uncharged atom* instead of successive electrons from the increasingly charged ion.

Though the technique is simple in principle, it is quite complex in practice. To obtain a 'spectrum' of photoelectron energies we first require a source of photons which all have the same energy (or frequency). Radiation of just one energy is called monochromatic radiation. With such a source of radiation, the photon energy, hf , in equation 9 is fixed. All that remains is to determine the kinetic energy of the electrons.

Can you suggest a means of doing this? Remember that photoelectrons, like ions, have charge and mass.

In Section 3 and in TV 10 we described how the mass of ions can be determined via their kinetic energy using a mass spectrometer. In the photoelectron experiment we shine monochromatic electromagnetic radiation on atoms. These atoms then emit photoelectrons, which have particular energies according to equation 9. These kinetic energies are determined in a similar way to the determination of the kinetic energies of ions in a mass spectrometer. Knowing the photon energy of the radiation, we can then estimate the ionization energies of the electron using equation 9.

In this way the energy levels of electrons in atoms can be examined directly; each peak in a photoelectron spectrum corresponds to ionization of an electron from an electron energy level. Figure 28 shows the simple relationship between the photoelectron spectrum of an atom with three occupied electron energy levels and the electron energy-level diagram for that atom. Notice that when the spectrum is rotated through 90° it gives a picture of the electron energy-level diagram.

According to equation 9 the ionization energy is the photon energy minus the kinetic energy of the ejected electron, and this relationship is demonstrated in Figure 28; the electron kinetic energy and the ionization energy increase in opposite directions.

Photoelectron spectroscopy contrasts with the spectroscopic technique you used

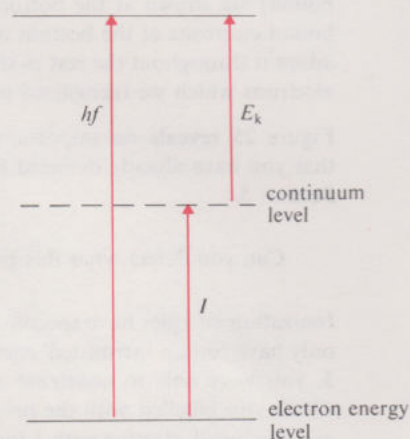


FIGURE 27 Relationship between I , E_k and hf .

in Section 5, in which each line in the spectrum represents the *difference* between two bound states of the electron in the atom. Photoelectron spectroscopy measures the difference between a bound state of the electron and the energy of a free electron at the continuum level. Since we are interested in investigating the electron energy levels of atoms, we shall restrict our attention to elements that exist conveniently (at ordinary temperatures) as separate atoms and not substances that consist of combinations of atoms. For our purposes, this limits us to a few gases which are minor components of the atmosphere—the noble gases. Hydrogen is in any case uninteresting because it contains only one electron, and you have already fully determined its electron energy-level diagram using emission spectroscopy in Section 5.

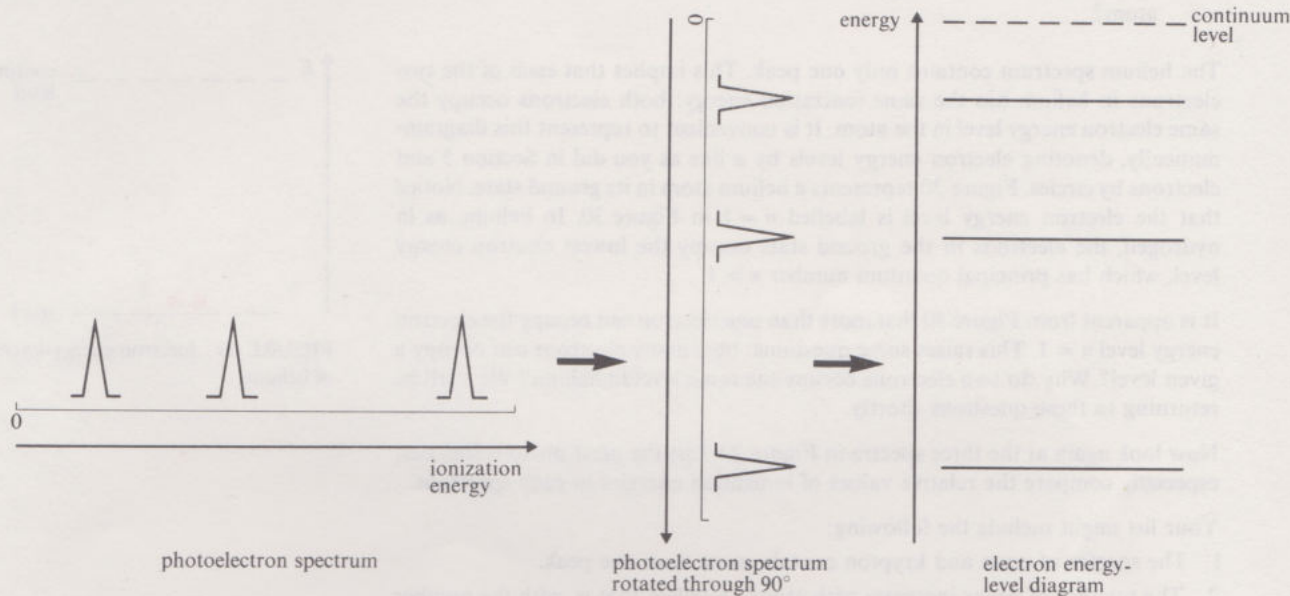


FIGURE 28 How to obtain the electron energy-level diagram from the photoelectron spectrum. The presence of a peak in the photoelectron spectrum indicates the emission of photoelectrons with a particular ionization energy.

The photoelectron spectra of three of the noble gases: helium, neon, and krypton, are shown in Figure 29. To ionize the tightly bound electrons in neon and krypton, radiation of very high photon energy is needed. We use X-rays. The energy scale for the krypton spectrum in Figure 29 is graduated in electron volts as well as the more familiar energy unit, the joule. In this type of experiment, results are conventionally reported in electron volts, since this is the kinetic energy acquired by an electron that has been accelerated by a potential difference of one volt. However, for easy comparison with other electron energy diagrams in these Units, we shall plot photoelectron spectra in joules.

To interpret these spectra you will need to know how many electrons are contained in each type of atom.

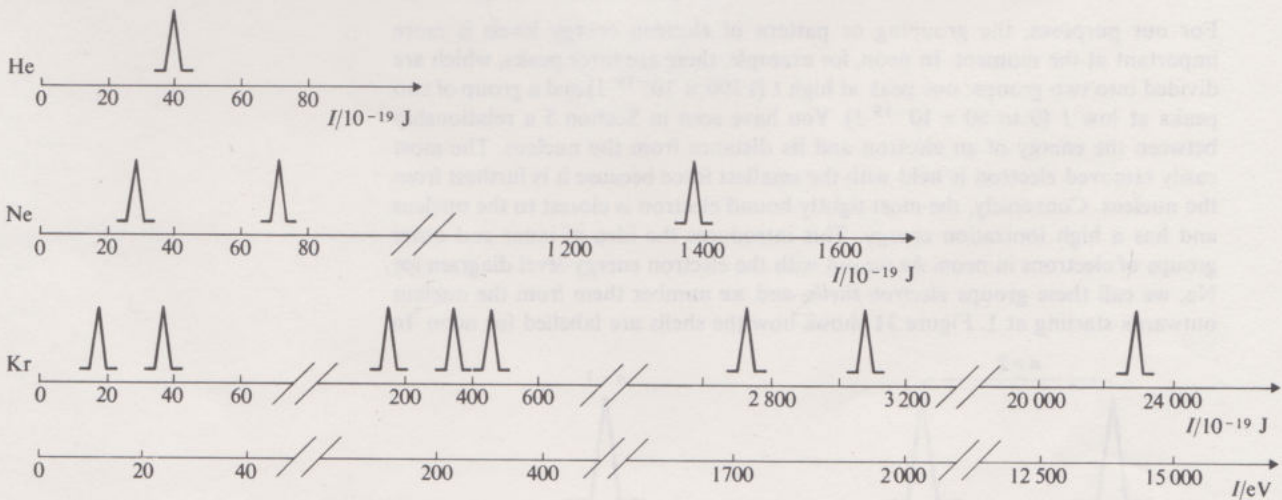


FIGURE 29 Photoelectron spectra of helium, neon and krypton: notice how the scales are broken and the large gaps that appear between the electron shells.

Where can you find this information?

Remember that the number of electrons is equal to the atomic number, and these are listed in Appendix 1.

Complete the table in the margin using the values of the atomic numbers.

Atom	Number of electrons
He	2
Ne	10
Kr	36

Obviously a lot of information is contained in the spectra in Figure 29. Concentrate on the most obvious features.

Look first at the spectrum of helium.

How many electron energy levels do the two electrons occupy in a helium atom?

The helium spectrum contains only one peak. This implies that each of the two electrons in helium has the same ionization energy: both electrons occupy the same electron energy level in the atom. It is convenient to represent this diagrammatically, denoting electron energy levels by a line as you did in Section 5 and electrons by circles. Figure 30 represents a helium atom in its ground state. Notice that the electron energy level is labelled $n = 1$ in Figure 30. In helium, as in hydrogen, the electrons in the ground state occupy the lowest electron energy level, which has principal quantum number $n = 1$.

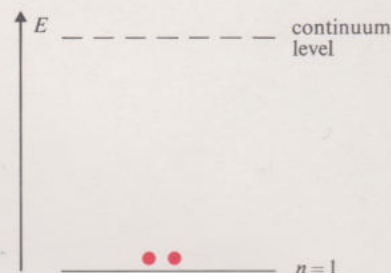


FIGURE 30 Electron energy-level diagram of helium.

It is apparent from Figure 30 that more than one electron can occupy the electron energy level $n = 1$. This raises some questions: how many electrons can occupy a given level? Why do two electrons occupy the same level in helium? We shall be returning to these questions shortly.

Now look again at the three spectra in Figure 29. List the most obvious features; especially compare the relative values of ionization energies in each spectrum.

Your list might include the following:

- 1 The spectra of neon and krypton contain more than one peak.
- 2 The number of peaks increases with atomic number, that is, with the number of electrons.
- 3 Within a spectrum the peaks fall into groups, each of which spans a relatively small range in the values of I (by less than a factor of three), for example the peaks in the range 150 to $450 \times 10^{-19} \text{ J}$ in the krypton spectrum. On the other hand, the energy differences between groups are considerably larger.

Using the electron energy-level model that we developed in Section 5, how can you account for the first two points above?

If an atom has more than one ionization energy, its electrons occupy different levels. Apparently, the number of levels that are occupied increases with the number of electrons. The most plausible explanation of this observation is that there is a limit to the number of electrons that can occupy any level, and as electrons are added they occupy higher levels. This explanation coincides with the shell interpretation of the successive ionization energies of sodium (Figure 25).

For our purposes, the grouping or pattern of electron energy levels is more important at the moment. In neon, for example, there are three peaks, which are divided into two groups: one peak at high I ($1390 \times 10^{-19} \text{ J}$) and a group of two peaks at low I (0 to $80 \times 10^{-19} \text{ J}$). You have seen in Section 5 a relationship between the energy of an electron and its distance from the nucleus. The most easily removed electron is held with the smallest force because it is furthest from the nucleus. Conversely, the most tightly bound electron is closest to the nucleus and has a high ionization energy. This introduces the idea of inner and outer groups of electrons in neon. As we did with the electron energy-level diagram for Na, we call these groups *electron shells*, and we number them from the nucleus outwards starting at 1. Figure 31 shows how the shells are labelled for neon. In

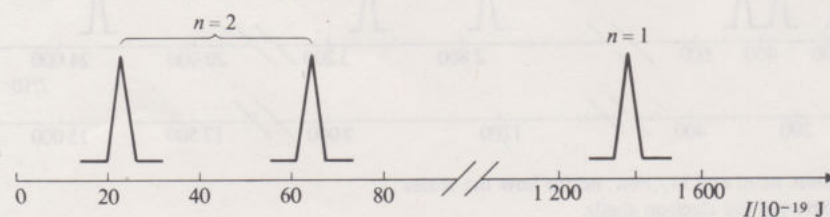


FIGURE 31 Electron shells in neon—as shown by its photoelectron spectrum.

fact these numbers are the principal quantum numbers that you used to label the energy levels derived from the spectrum of hydrogen. The relationship between the photoelectron spectra in Figures 29 and 31 and an electron energy-level diagram is again immediately obvious if you turn the page through 90° so that the spectra are arranged vertically with the $n = 1$ level at the bottom and $l = 0$ at the top.

Now label the groups of peaks in the spectrum of krypton (Figure 29) with their principal quantum numbers, n .

Your labels should be the same as the values of n in Figure 52 on p. 74. Ignore for a moment the values of l .

Viewed as electron energy-level diagrams, the spectra in Figure 29 show that, roughly speaking, these atoms have a pattern of energy levels similar to hydrogen, although in hydrogen only the lowest level ($n = 1$) is occupied in the ground state. But notice that electrons in the inner shells are more tightly held as the atomic number increases. This is exactly what we would expect because the nuclear charge is directly proportional to the atomic number.

Another difference is apparent if you compare the spectra in Figure 29 with the energy-level diagram for hydrogen (Figure 21).

What is this difference?

In hydrogen each of the quantum numbers describes a *single* electron energy level. As the photoelectron spectra show, this is not true for other atoms. The electron shells consist of a number of electron energy levels, which we call *sub-shells*. The spectrum of krypton gives us most information about sub-shells.

How many sub-shells are there in each of the electron shells $n = 1$ to $n = 3$?

$n = 1$	sub-shells =	?
$n = 2$	sub-shells =	?
$n = 3$	sub-shells =	?

For these three electron shells there appears to be a relationship between the number of sub-shells and the principal quantum number, but you may be wondering why Figure 29 does not show *four* sub-shells in the electron shell $n = 4$. In fact there are four, but in krypton only two of these sub-shells contain electrons; the other two are empty. So we have a simple rule, derived from the photoelectron spectra, but which can also be established theoretically. *The number of sub-shells in any electron shell is equal to the principal quantum number of that electron shell.*

In Section 5 we introduced the principal quantum number as a means of labelling the electron energy levels in hydrogen. The value of n describes completely the electron energy level occupied by an electron in hydrogen, but it fails to do this for all other atoms. To describe the sub-shell structure we need a *second quantum number*. This quantum number is given the symbol l . Like the principal quantum number, l is given values corresponding to the energy of the sub-shell, but for theoretical reasons that are beyond the scope of these Units the lowest value that l is given is zero. So for any particular shell, the sub-shells are numbered from zero to $(n - 1)$.

What are the possible values that l can have for the third and fourth electron shells?

For $n = 3$, l can have values 0, 1 and 2. There are three sub-shells, as you saw in the spectrum of krypton.

For $n = 4$, l can have values 0, 1, 2 and 3. There are four sub-shells, although in krypton only the first two of these are occupied, that is, $l = 0$ and $l = 1$.

Notice that the lowest value of l is given to the sub-shell with the lowest energy. Thus, in neon the levels can be labelled as in Figure 32. Of course, this diagram reflects exactly the electron energy levels that are revealed by photoelectron spectroscopy (Figure 29).

As we said earlier, a lot of information is contained in the spectra in Figure 29.

electron sub-shell

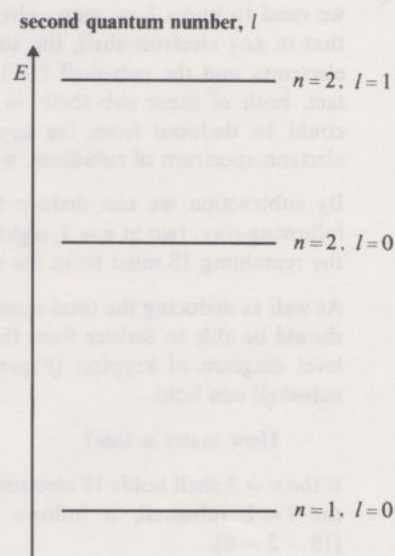


FIGURE 32 Electron energy-level diagram for neon (not drawn to scale), showing the levels labelled by quantum numbers n and l .

Implicit in the observation that the number of occupied levels or sub-shells increases with atomic number is the idea that electrons fill the lowest electron energy levels first. You would, of course, expect atoms to adopt the most stable arrangement, with their electrons in the lowest electron energy levels. Since you also know the number of sub-shells (l value) in any shell (any value of n), you have almost enough information to draw a diagram showing which levels the electrons occupy—but not quite.

What further information do you need?

So far we have said very little about the *number* of electrons that can occupy each level.

It is not easy to determine how many electrons can be contained in each particular level using information from photoelectron spectroscopy. It can be established from a mathematical model of the atom such as that used to obtain Figure 12. However, you already have a clue to the number of electrons in any level, or the *occupancy* of the level from the results of an experiment.

Look at Figure 26, which shows the electron energy shells of sodium.

How many electrons can be accommodated in the electron shells

$$n = 1?$$

$$n = 2?$$

There are 2 (in $n = 1$) and 8 (in $n = 2$). Remember that in sodium the $n = 3$ shell is not full. Now from Figure 32 you can also see that the $n = 2$ electron shell is divided into two sub-shells, $l = 0$ and $l = 1$. Since the single shell in helium ($n = 1$, $l = 0$) holds two electrons, it seems reasonable to assume that the $n = 2$, $l = 0$ sub-shell in sodium also holds a maximum of two electrons. In fact, all sub-shells with $l = 0$ can hold a maximum of two electrons.

Now complete the table in the margin by writing the maximum number of electrons in each of the sub-shells in the first two quantum shells.

Shell	Sub-shell	Number of electrons
$n = 1$	$l = 0$	
$n = 2$	$l = 0$	
$n = 2$	$l = 1$	

The missing numbers are respectively 2, 2 and 6. Earlier we raised the questions: why does the $n = 1$ shell hold two electrons? and why does the $n = 2$ shell hold eight electrons? We can now add another question to these two questions: Why does the $n = 2$ shell consist of two sub-shells, which hold two and six electrons, respectively?

If you look at the photoelectron spectrum of krypton (Figure 29), you can obtain further information about the $n = 3$ quantum shell. The atomic number of krypton is 36, and the atom contains electrons in the $n = 1$, $n = 2$, $n = 3$ and $n = 4$ quantum shells.

How can we find out how many electrons are in the $n = 3$ quantum shell? First we need to know how many electrons are in the other shells. We can assume that in any electron shell, the sub-shell $l = 0$ can contain a maximum of two electrons, and the sub-shell $l = 1$ can contain a maximum of six electrons. In fact, both of these sub-shells in the $n = 4$ electron shell are *full*, a fact that could be deduced from the appearance of another sub-shell in the photoelectron spectrum of rubidium, which has one more electron than krypton.

By subtraction we can deduce that the $n = 3$ shell holds 18 electrons, in the following way: two in $n = 1$, eight in $n = 2$, eight in $n = 4$ (total: 18 electrons). So the remaining 18 must be in the $n = 3$ shell.

As well as deducing the total number of electrons in the $n = 3$ quantum shell, you should be able to deduce from the photoelectron spectrum and electron energy-level diagram of krypton (Figures 29 and 52), how many electrons the $l = 2$ sub-shell can hold.

How many is this?

If the $n = 3$ shell holds 18 electrons, including two in the $l = 0$ sub-shell and six in the $l = 1$ sub-shell, it follows that the $l = 2$ sub-shell holds ten electrons ($18 - 2 - 6$).

We now have almost enough information to predict the distribution of electrons in the shells and sub-shells of any atom. This distribution is called the *electronic*

electronic configuration

configuration of an element. A few diagrams will make it clear that this facility has been developed by the discussion so far and help us to introduce a shorthand method of writing electronic configuration.

Figure 33 shows the electron energy-level diagrams for several elements, with the electrons (depicted as red spots) already inserted in the diagram for sodium.

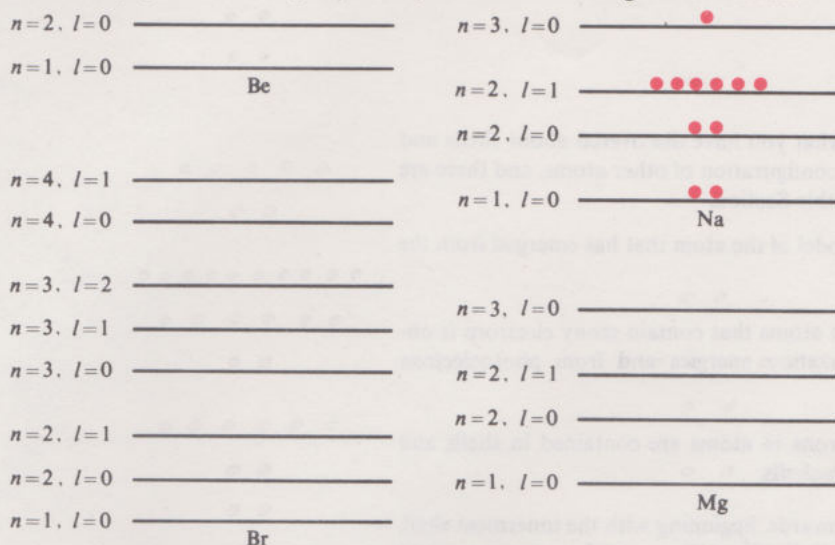


FIGURE 33 Energy-level exercise for some atoms.

Complete the diagrams for the other elements and compare your results with Figure 53 on p. 74.

Before we proceed to establish and apply the rules for determining the electronic structures of more complicated atoms, it will be convenient to represent the sub-shells using a shorthand notation instead of drawing diagrams.

6.1 The s-p-d-f notation

Electronic structures were originally established by the spectroscopic technique you used in Section 5. In the emission spectrum of sodium the lines appear as several series, one of which consists of *sharp* lines and another of *diffuse* lines. A third series was regarded as the *principal* series, since it is the most intense. The value of the second quantum number is usually denoted by the initial letters of these series, *s*, *p*, *d* and *f* (*f* comes from fundamental), so instead of using numbers for particular values of l , we can write:

- s for sub-shells with $l = 0$
- p for sub-shells with $l = 1$
- d for sub-shells with $l = 2$
- f for sub-shells with $l = 3$

These letters can be used as a shorthand method of labelling electron energy levels. The singly occupied level in hydrogen has $n = 1$, $l = 0$. So it is said to be a 1s level. 1 denotes the value of n , and s denotes the value of l .

Label the levels in Figure 32 using this notation.

The three levels are shown labelled in Figure 34 on p. 50.

The same notation is used to represent the electronic configuration. For example, helium has two electrons in the 1s level. We say that it has two 1s electrons and we show the number of electrons using a superscript on the s. The electronic configuration of helium is written

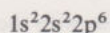
$$1s^2$$

and this is spoken as 'one s two'. Similarly, the electronic configuration of other atoms can be written in this shorthand notation.

Taking account of the information in Figure 34, write the electronic configuration of neon using the s-p-d-f notation.

s-p-d-f notation

The electronic configuration is simply a statement of the way that the electrons are distributed among the sub-shells, and these are usually written in order of increasing values of n . The electronic configuration of neon is



6.2 Summary of Section 6

You are now in a position to apply what you have discovered about shells and sub-shells to determine the electronic configuration of other atoms, and there are some SAQs testing this at the end of this Section.

Again it is useful to summarize the model of the atom that has emerged from the discussion in Section 6.

1 Information about the electrons in atoms that contain many electrons is obtained by measuring successive ionization energies and from photoelectron spectroscopy.

2 These techniques show that electrons in atoms are contained in shells and each shell consists of one or more sub-shells.

3 The shells are numbered from 1 upwards, beginning with the innermost shell, which contains the most tightly bound electrons. These numbers correspond to the principal quantum number (n) used to label the levels in the hydrogen atom.

4 A shell with principal quantum number n , consists of n sub-shells, which are labelled by a second quantum number, l . l can have values from zero to $(n - 1)$. The values of l are denoted by the letters s, p, d and f, corresponding to $l = 0, 1, 2$ and 3, respectively.

5 Each sub-shell can contain a limited number of electrons: two in an s sub-shell, six in a p and ten in a d.

Now that you have completed Section 6 you should be able to do the following things:

Show that you have some idea of what is meant by the terms: 'electron shell', 'successive ionization energies', 'photoelectron spectroscopy', 'photoelectron', 'electron sub-shell', 'second quantum number, l ', 'electronic configuration', 'electronic structure', 's-p-d-f notation'.

Represent or interpret on an electron energy-level diagram the energy jumps corresponding to:

- absorption spectra;
- emission spectra;
- first ionization;
- photoelectron spectra.

Estimate roughly the ionization energy of an atom, using the electron energy-level diagram derived from atomic spectra.

Describe and identify experimental evidence for the existence of electron shells and sub-shells.

Relate this evidence to the quantization of electron energy in the atom and describe this quantization by quantum numbers.

To test your achievement of the above Objectives, try the following SAQs.

SAQ 23 Figure 35 shows an electron energy-level diagram of an atom of the hypothetical element pandemonium. In the ground state, only levels X and Y are occupied by electrons and both levels are fully occupied. Use arrows to represent the energy changes corresponding to:

- an absorption line in the spectrum;

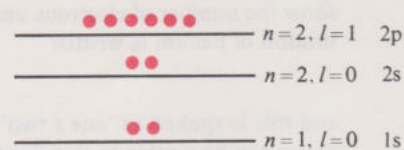


FIGURE 34 Notation for electronic configuration, for example for neon.

- (b) an emission line in the spectrum;
- (c) ionization energy of an electron in the level Y;
- (d) the ejection of a photoelectron produced by a photon of 4 arbitrary energy units.

SAQ 24 Using the information in SAQ 23 and in Figure 35, estimate the lowest ionization energy of the element pandemonium.

SAQ 25 Figure 36 shows the photoelectron spectrum of magnesium. Identify the electron sub-shells corresponding to each of the ionization energies and decide how many electrons are in each sub-shell (an atom of magnesium contains 12 electrons).

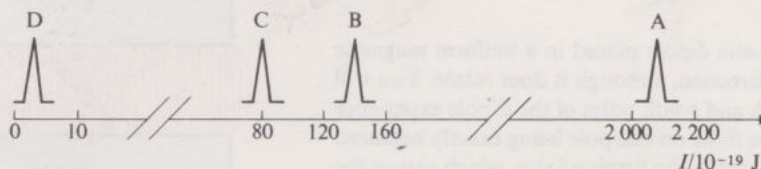


FIGURE 36 Photoelectron spectrum of magnesium.

SAQ 26 Figure 37 is the photoelectron spectrum of the gas argon, which exists as single atoms. What evidence is contained in this spectrum for the existence of electron shells and sub-shells?

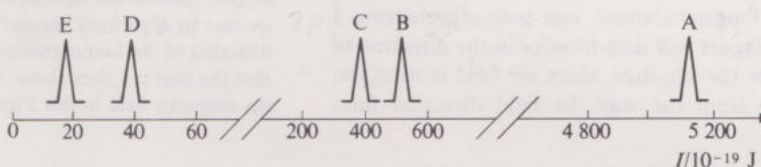


FIGURE 37 Photoelectron spectrum of argon.

SAQ 27 Using the information in Figure 37, sketch an electron energy-level diagram for argon. Label the levels with values of the principal quantum number and the appropriate letter to denote the second quantum number, using the convention given in Section 6.1.

In Section 6 we have examined the shell and sub-shell structure of atoms, and the rules governing electron distribution among the sub-shells. However, we have not attempted to explain these rules. For example:

Why does the $n = 1$ shell contain two electrons? Why do sub-shells contain different maximum numbers of electrons?

These questions can be answered by examining more closely the emission spectra of elements and the way that atoms behave in magnetic fields. We do this in the next two Sections before developing some general rules for establishing electronic configuration.

7 Electron spin

Let us first turn our attention to the $n = 1$ shell.

Why should this shell be capable of accommodating two, and no more than two, electrons?

Here are some experimental clues. Can they help us answer the question?

- (a) When a beam of hydrogen atoms is passed through an inhomogeneous (non-uniform) magnetic field, it splits into two beams.
- (b) The same experiment performed on a stream of helium atoms produces no deflection of the beam.

All we can say straight away as a result of this information is that hydrogen atoms have magnetic properties that helium atoms do not have.

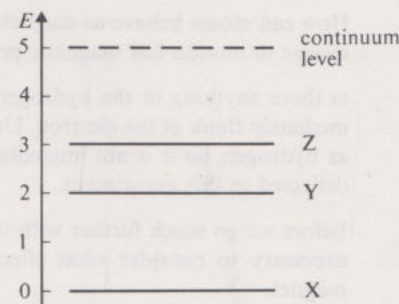


FIGURE 35 Electron energy-level diagram for the element pandemonium. (The energy scale is marked in arbitrary energy units.)

How can atoms behave as magnets? Well, you know from Unit 5 that an electric charge in motion has magnetic properties.

Is there anything in the hydrogen atom that answers this description? We immediately think of the electron. Unfortunately, helium has twice as many of these as hydrogen, so it is not immediately obvious why helium atoms should not be deflected in this experiment.

Before we go much further with interpreting the information in (a) and (b), it is necessary to consider what effect a *non-uniform* magnetic field has on a bar magnet.

7.1 Uniform and non-uniform fields

In Unit 5 it was explained that a magnetic dipole placed in a uniform magnetic field does not move bodily in a given direction, although it does rotate. You will remember that this is because the north and south poles of the dipole experience equal attraction in the uniform field, the force on one pole being exactly balanced by the force on the other. All that remains is the turning force, which causes the dipole to rotate in order to align itself with the magnetic field (Figure 38) Once it is aligned, it stays put.

If the magnetic field changes significantly over a distance comparable with the range of observation, it is said to be non-uniform. In this case the forces on opposite poles of the magnet are no longer balanced, one pole experiencing a stronger force than the other, so the magnet will tend to *move* in the direction of the stronger force. Figure 39 illustrates the situation when the field is strongest near the north pole, as can be seen from the way the field direction lines crowd together at the north pole.

You will remember from your experiments in Unit 5 that magnetized objects such as iron filings and paper clips move in this way when subjected to a non-uniform field (for example a bar magnet).

7.2 Electron spin

In the experiment whose results we presented in observations (a) and (b) above, the geometry of the magnet is like that in Figure 39. One of the pole pieces is a knife-edge, the other a groove, and the magnet pole faces are relatively long, as shown in Figure 40. The field strength at the knife edge is very much higher than at the groove. Any atomic magnets passing through this very non-uniform field are subject to a deflecting force.

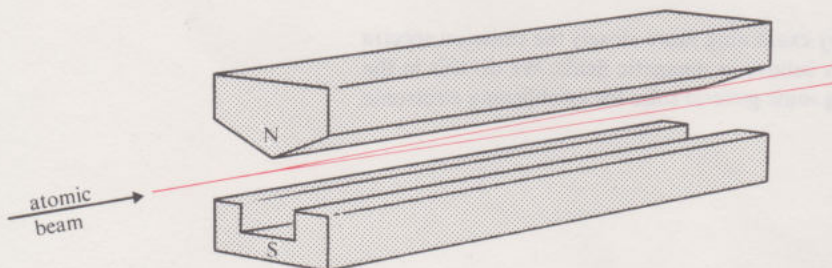


FIGURE 40 The splitting of an atomic beam by a magnetic field.

What conclusion can we draw from the information that a beam of hydrogen atoms splits into two under these circumstances?

It seems that a random sample of hydrogen atoms behaves as though it contains *two* kinds of magnet, which are deflected differently in the non-uniform field. As one beam is deviated towards the knife-edge, and the other away from it, it appears that the two atomic magnets interact in opposite senses with the applied field.

Let us now consider what motion of the electron could be responsible for the magnetic properties of the hydrogen atom. If we suppose that the electron is orbiting the nucleus, it behaves as a current loop, which has an associated dipole (Unit 5). However, you know from Figure 12 that the electron distribution in the

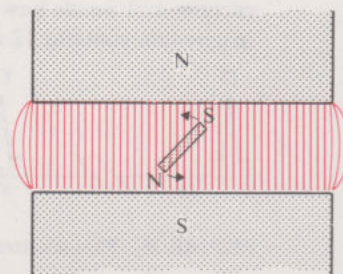


FIGURE 38 A bar magnet in a uniform (homogeneous) magnetic field. The curved arrows indicate the tendency of the bar magnet to align itself parallel to the direction of the homogeneous field. (Note that the thin red lines show the direction of the magnetic field in this Figure.)

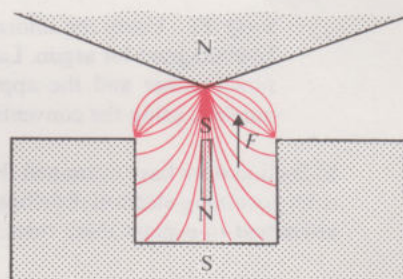


FIGURE 39 A bar magnet in a non-uniform (inhomogeneous) magnetic field. F is the net force that tends to move the bar magnet towards the point at which the magnetic field is the strongest, that is, the north pole in this case. (Note that as in Figure 38, the thin red lines show the direction of the magnetic field.)

hydrogen atom is spherical, so all directions of alignment of the dipole are equally probable. On average, therefore, the magnetic effects of the dipoles will cancel.

If the magnetism does not result from orbiting motion of the electron, it must be the consequence of motion *in* the electron. There seems to be some kind of internal circulation of the charge carried by the electron. We can think of this as *spin*: rotation of the electron about its own axis. This rotation is, in effect, a loop of electric current, which produces a magnetic field.

The splitting of the beam in two directions indicates that there are just two ways the electron can spin; we can think of these as being clockwise or anticlockwise (Figure 41). The magnetic field produced by a clockwise-spinning electron will have opposite polarity to that produced by an anticlockwise-spinning electron, because it corresponds to an electric current in the opposite direction (Section 5.2 of Unit 5).

electron spin

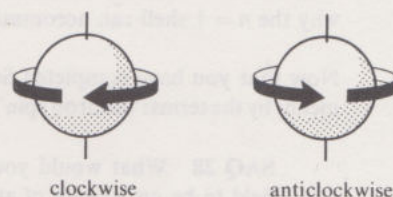


FIGURE 41 The spinning electron.

Now suggest what the two beams observed in experiment (a) for hydrogen atoms might correspond to.

One beam must be due to atoms with clockwise-spinning electrons, and the other to atoms with anticlockwise-spinning electrons.

There is an equal probability that the single electron in any hydrogen atom has either kind of spin. In the absence of a magnetic field, the energy of the electron is independent of the direction of its spin. Only the application of the field reveals the existence of the different 'states of spinning'. As Figure 42 shows, the anticlockwise spinning electron has a slightly different energy in the field from the one spinning clockwise.

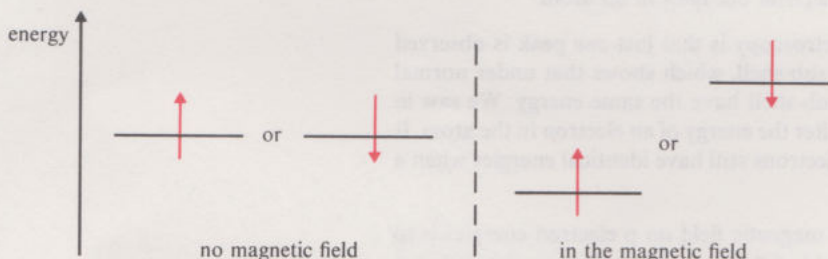


FIGURE 42 The effect of a magnetic field on the spinning electron of the hydrogen atom. The upward- and downward-pointing arrows indicate the clockwise and anticlockwise spin of the electron.

What conclusion can you now draw from the observation that helium atoms are undeflected by the non-uniform field?

A helium atom has *two* electrons in the 1s level. The absence of magnetism can only be explained by assuming that the two electron 'magnets' have opposite polarity, so that they cancel each other out. In other words, the two electrons in the $n = 1$ quantum shell must have opposite spins. We say that the spins are '*paired*'.

pairing of electrons

When we study the magnetic behaviour of other atoms, we discover that the 'pairing' of electron spins in the helium atom is part of a general phenomenon. We can represent the electronic structure of helium ($1s^2$) by depicting the two 'paired' electrons as half-headed arrows in a box representing the sub-shell



The spin of an electron can also be indicated by another quantum number, the *spin quantum number* s , which can have values $+\frac{1}{2}$ or $-\frac{1}{2}$.

spin quantum number, s

Atoms containing only full quantum shells (or sub-shells) of electrons have no magnetic properties. This means that all electron spins must be paired when a quantum shell (or sub-shell) is full.

We have now gone some way to answer the question asked at the start of this section, namely why are there just two electrons in the $n = 1$ quantum shell? We now know that this shell consists of *one* sub-shell, which can accommodate only two electrons with opposite spin. In the helium atom, where the $n = 1$ quantum shell is full, with two electrons, the photoelectron spectrum shows that there is just one energy level corresponding to this one sub-shell.

7.3 Summary of Section 7

A beam of hydrogen atoms is split into two beams by an inhomogeneous magnetic field. This observation indicates that the atom behaves as a magnet, a suggestion which is explained by assuming that the electron in the atom spins in one of two directions, clockwise or anticlockwise. The spin quantum number, s , is introduced to describe the electron spin (as $s = +\frac{1}{2}$ or $s = -\frac{1}{2}$), and to explain why the $n = 1$ shell can accommodate just two electrons.

Now that you have completed Section 7, you should have some idea of what is meant by the terms: 'electron spin', 'pairing of electrons', 'spin quantum number, s '.

SAQ 28 What would you expect the effect of a non-uniform magnetic field to be on a beam of atoms of (i) Ne, (ii) Na, (iii) Kr?

8 Degeneracy and sub-shells

The question that we have to consider next is slightly more complex. Why should a p sub-shell be able to hold six electrons? Does this mean that for some as yet unknown reason, there is one orbital which can hold six electrons? Or does it mean that the p sub-shell consists of several orbitals? Remember that 'orbital' is the name given to the space that an electron occupies in an atom.

The evidence from photoelectron spectroscopy is that just *one* peak is observed corresponding to ionization from a p sub-shell, which shows that under normal conditions all six electrons in the p sub-shell have the same energy. We saw in Section 7.2 how a magnetic field can alter the energy of an electron in the atom. It might be interesting to see if the six electrons still have identical energies when a magnetic field is applied.

One way to investigate the effect of a magnetic field on p electron energies is to look at the behaviour in a magnetic field of the $p \rightarrow s$ transition in the emission spectrum of a suitable atom. It is best to avoid complicating effects due to electron spin, so we choose an atom where the highest occupied level in the ground state is a full s level.

The atom we have chosen is magnesium, which has a full s sub-shell and in which the lowest unoccupied level is a p level. You will remember that its ground-state configuration is $1s^2 2s^2 2p^6 3s^2$ (SAQ 25). A strong line at 1.05×10^{15} Hz (in the ultraviolet) has been identified as corresponding to a transition from an excited state, where an electron is in the 3p sub-shell, to the ground state.

When the emission spectrum of magnesium is obtained in a very strong magnetic field (stronger by a factor of about 1000 than anything the magnets in your Kit can do) a tiny splitting of the line is observed. Under careful examination the line at 1.05×10^{15} Hz is seen to consist of three closely spaced lines.

What do you infer from the appearance of three lines in place of one?

The p sub-shell (occupied in the excited state), which consisted of just one electron energy level in the absence of a magnetic field, must consist of *three* levels in a magnetic field.

This is a very significant result, first observed by P. Zeeman in 1896, and is called the *Zeeman effect*. It shows that the p sub-shell is actually made up of *three* levels, which have identical energies in the absence of a magnetic field. We describe two or more electron energy levels that have the same energy as *degenerate* levels. As Figure 43 shows, these degenerate levels are differentiated only in a magnetic field. The three p levels can each contain two electrons.

Zeeman effect

degeneracy

It now begins to look as though the maximum number of electrons that any level can contain is two. If a sub-shell can hold more than two electrons, this is because the sub-shell consists of several degenerate levels. These levels can be differentiated only in a magnetic field.

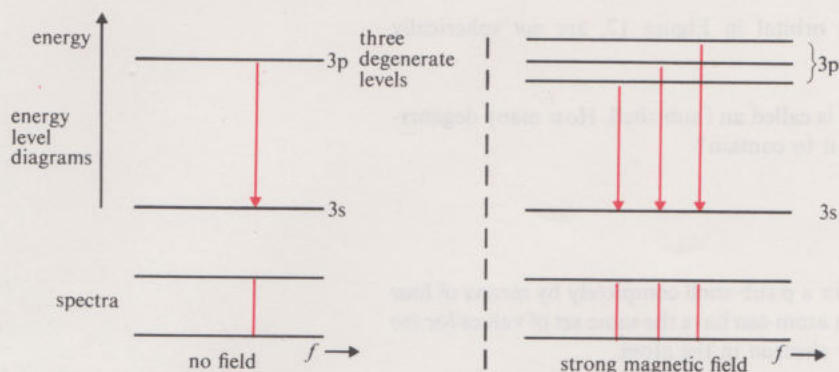


FIGURE 43 Splitting of $p \rightarrow s$ transition for magnesium in a strong magnetic field.

Cautionary note

At this point we have a confession to make. In presenting evidence about interaction of electron magnets with applied magnetic fields, we have deliberately chosen the very simplest cases. For example, we were careful to avoid discussion of the effect of a magnetic field on the $p \rightarrow s$ transition in an atom like sodium (ground-state configuration $1s^2 2s^2 2p^6 3s^1$), where the atom has a magnetic effect due to spin of the unpaired electron.

Magnetism due to electron *spin* can interact with that due to electron *orbital motion* to produce highly complex splitting patterns for some atoms in a magnetic field. We have chosen examples where magnetic effects are due to *either spin or orbital motion* and not a combination of both.

SAQ 29 What effect would you expect application of a magnetic field to have on the spectral line from the $2s^1 \rightarrow 1s^1$ transition in hydrogen?

SAQ 30 What effect would you expect application of a strong magnetic field to have on the transition of a helium atom from the electronic configuration $1s^1 2s^1$ to the electronic configuration $1s^2$? (You may assume there is no magnetic effect due to electron spin in the excited state.)

SAQ 31 If a stream of beryllium atoms were passed through an inhomogeneous magnetic field, what effect would you expect to see?

8.1 The magnetic quantum number

We now need to introduce yet another quantum number to distinguish the individual degenerate levels within each sub-shell.

You will remember from Section 6 the values that the second quantum number has for s, p and d sub-shells.

An s sub-shell with quantum number $l = 0$ contains just one orbital.

A p sub-shell with quantum number $l = 1$ contains three degenerate orbitals.

A d sub-shell with quantum number $l = 2$ contains five degenerate orbitals.

You probably begin to see a pattern here. The number of degenerate orbitals is $2l + 1$ in all cases.

The quantum number that we use to label the degenerate levels that make up p or d sub-shells is called the *magnetic quantum number* and is given the symbol m . We choose the quantum numbers so that they span the integers between $+l$ and $-l$. Thus, the three orbitals in the p shell ($l = 1$) are numbered $m = +1$, $m = 0$, $m = -1$.

magnetic quantum number, m

What magnetic quantum numbers identify

- (i) the one orbital in the s sub-shell
- (ii) the five orbitals in the d sub-shell?

(i) $m = 0$

(ii) $m = +2, m = +1, m = 0, m = -1, m = -2$.

We do not propose at this stage to go into the reason why p orbitals are affected by a magnetic field. We can merely indicate that it is connected with the fact that

the p and d orbitals, unlike the s orbital in Figure 12, are *not* spherically symmetric.

SAQ 32 The shell with $l = 3$ is called an f sub-shell. How many degenerate orbitals would you expect it to contain?

8.2 Four quantum numbers

We can now describe each electron in a p sub-shell completely by means of four quantum numbers. No electron in an atom can have the same set of values for the four quantum numbers as any other electron in the atom.

Describe all six 2p electrons by listing their quantum numbers.

All six have $n = 2$.

All six have $l = 1$.

Writing the electrons in pairs, with opposite spin:

$$n = 2, \quad l = 1, \quad m = -1, \quad s = +\frac{1}{2}$$

$$n = 2, \quad l = 1, \quad m = -1, \quad s = -\frac{1}{2}$$

$$n = 2, \quad l = 1, \quad m = 0, \quad s = +\frac{1}{2}$$

$$n = 2, \quad l = 1, \quad m = 0, \quad s = -\frac{1}{2}$$

$$n = 2, \quad l = 1, \quad m = +1, \quad s = +\frac{1}{2}$$

$$n = 2, \quad l = 1, \quad m = +1, \quad s = -\frac{1}{2}$$

You will see in Section 9 how this procedure can be applied to describe the electronic configurations of any atom.

SAQ 33 How many electrons do you now expect the $n = 3$ shell to be capable of accommodating?

8.3 Summary of Section 8

In Sections 7 and 8 we have examined two experiments that complete our description of electrons in atoms by introducing two more quantum numbers.

To account for the fact that when a beam of hydrogen atoms is passed through an inhomogeneous magnetic field it splits into two beams, we said that an electron in an atom spins in a clockwise or an anticlockwise direction. This quantization of electron spin is expressed in terms of the spin quantum number, s . Since the only values of s are $+\frac{1}{2}$ and $-\frac{1}{2}$, the $n = 1$ shell can only accommodate two electrons.

A p sub-shell can accommodate six electrons because the sub-shell consists of three orbitals of equal energy (degenerate), each capable of holding two electrons. Evidence for this degeneracy is found when atomic spectra are produced in a strong magnetic field; in the magnetic field the degenerate levels are separated into levels of different energy. The degenerate levels are labelled with the magnetic quantum number m , which has values from $-l$ to $+l$.

Each electron in an atom can therefore be labelled by four quantum numbers, n , l , m and s , which distinguishes it from all other electrons in the atom.

Now that you have completed Section 8, you should have some idea of what is meant by the terms: 'the Zeeman effect', 'degeneracy', 'magnetic quantum number, m '.

9 Electronic configurations of the elements

We are now in a position to draw together the ideas that we have developed about electron energy levels and quantum numbers in order to establish the electronic configurations of the elements. If you are wondering why we have spent so much time on this aspect of atomic structure, remember what we said at the start of this

discussion: not only is our knowledge of atomic structure a fascinating result of man's curiosity, but the chemistry of the elements is very dependent on their electronic structures. A knowledge of electronic structure is often a useful aid to remembering, understanding and sometimes to predicting the chemical behaviour of elements.

At this stage you should be able to write the electronic structure of the atom of any element up to atomic number 18, argon, using the appropriate sequence of electron sub-shells: 1s, 2s, 2p, 3s, 3p, and remembering the degeneracy of the levels. Here is a summary of the rules for writing electronic configurations:

- In the ground state the electrons fill the innermost (lowest energy) shells first.
- The sequence of electron shells is determined mainly by the principal quantum number, n , which can have values 1, 2, 3, etc.
- The electron shells designated by the principal quantum number are divided into sub-shells, designated by the second quantum number, l .
- The number of sub-shells is equal to the value of the principal quantum number (because l has values 0, 1, 2, ... up to $(n - 1)$).
- Within a quantum shell, the energies of the sub-shells increase with the value of the second quantum number, l .
- There is a maximum number of electrons that any sub-shell can hold:
 - $l = 0$, s : two electrons
 - $l = 1$, p : six electrons
 - $l = 2$, d : ten electrons

Provided you know the order of filling electron sub-shells for an element, you should be able to write the electronic configuration using these rules.

Try this for the elements oxygen and sulphur. Their atomic numbers are 8 and 16, respectively.

If you have followed the procedure correctly, you should have written the following:

oxygen $1s^2 2s^2 2p^4$
 sulphur $1s^2 2s^2 2p^6 3s^2 3p^4$

Now repeat the procedure for manganese (atomic number 25).

If you have followed the rules, you have probably written:

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

If you wrote this, you have correctly applied the procedure for filling the sub-shells with electrons, but you have probably assumed that the 3d sub-shell fills before the 4s sub-shell. In fact this assumption is *wrong*. As you know from the electron energy-level diagram for hydrogen (Figure 21) or for any other atom, the energies of the *electron shells* converge as n increases. Also, as you can see from the Ne and Kr photoelectron spectra (Figure 29), the separation in energy of the s, p and d *sub-shells* within any shell separate as the elements get heavier. A consequence of this is that the 4s sub-shell is actually filled before the 3d. The correct electronic configuration for manganese is then:

Mn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

and the electron energy-level diagram is as shown in Figure 44. Note that although the 4s sub-shell is filled before the 3d, it is still correct to write the electronic configuration in the order shown.

In representing the electronic configuration of an element in the way shown above for manganese, you indicate the electron occupancy of the energy levels and also the first two quantum numbers, n and l , of each of the electrons in the atom. The electronic structure of an atom can be represented in a slightly different and more informative way in which the spin and magnetic quantum numbers are also depicted. This is done by representing each orbital as a box, and by representing the electron as an arrow pointing up or down to indicate its spin.

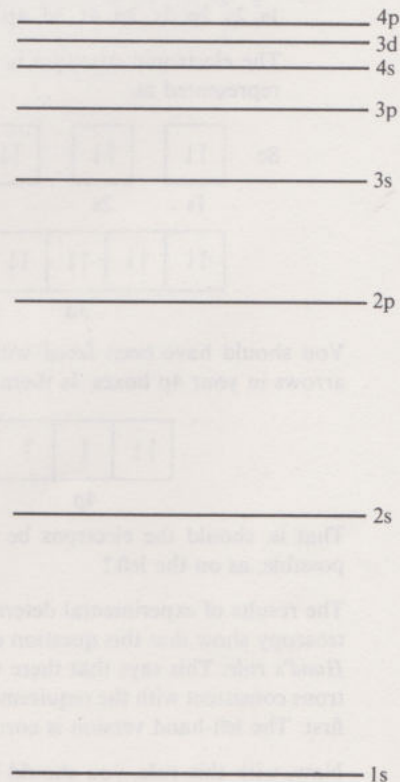
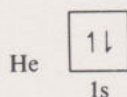


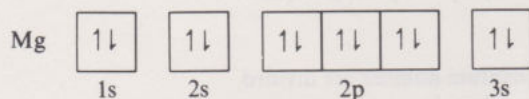
FIGURE 44 Electron energy-level diagram for manganese.

To take one of the simplest cases, helium, the 1s orbital is represented by a single box, and two arrows represent the electrons:



Notice that this form of representation vividly shows the 'pairing' of the electrons in the 1s orbital of helium.

To give you another example of this 'box' system of showing electronic configuration, the magnesium atom, which has the electronic structure $1s^2 2s^2 2p^6 3s^2$, is represented as:



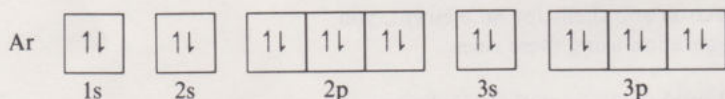
Notice that within each orbital the electron spins are paired.

9.1 Hund's rule

Note that we have single boxes for 1s and 2s, since they each contain only one pair of electrons, and a triple box for 2p because the 2p level is degenerate.

Use this system to show the electronic structure of argon (atomic number 18).

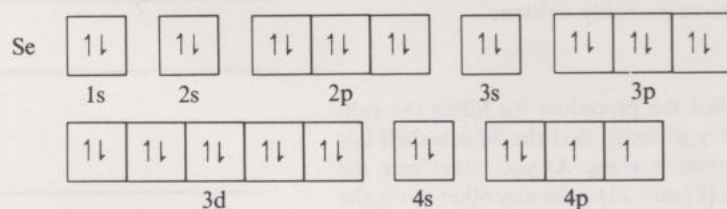
The electronic structure of argon is $1s^2 2s^2 2p^6 3s^2 3p^6$, and so it can be depicted as



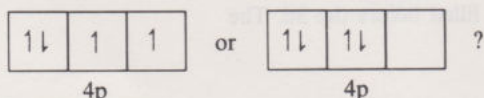
A d sub-shell can contain ten electrons, that is, five pairs, and is represented by a five-compartment box.

Now try to write out the electronic configuration of selenium, using the 'box' system. Its atomic number is 34. The order of filling the sub-shells is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p.

The electronic structure is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$, so the structure is represented as:



You should have been faced with a dilemma when you attempted to put the arrows in your 4p boxes. Is there any way of deciding whether to write



That is, should the electrons be *paired*, as on the right, or be left unpaired if possible, as on the left?

The results of experimental determinations of electronic configurations by spectroscopy show that this question can be answered by an empirical rule known as *Hund's rule*. This says that there will be the maximum number of *unpaired* electrons consistent with the requirement that the sub-shells of lowest energy are filled first. The left-hand version is correct in this case.

Hund's rule
unpaired electrons

Now, with this rule, you should be able to write the electronic structure of the atoms of any element, given the correct sequence of sub-shells. Figure 45 shows the order in which all the sub-shells are filled: you merely follow the snake.

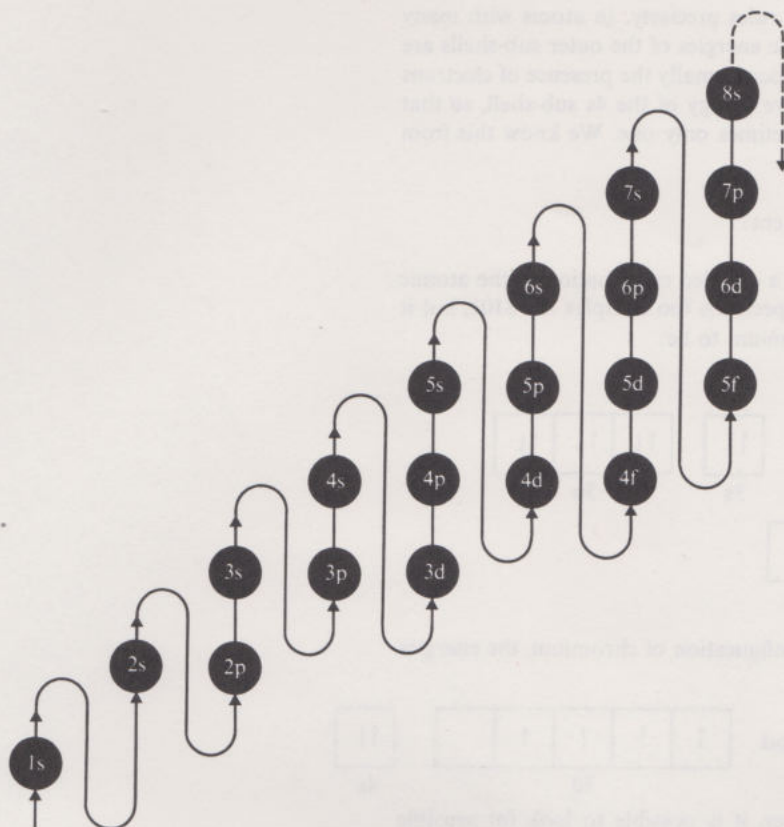
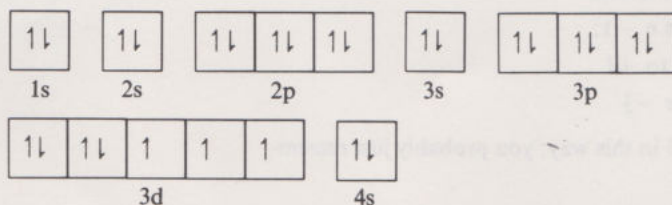
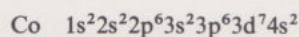
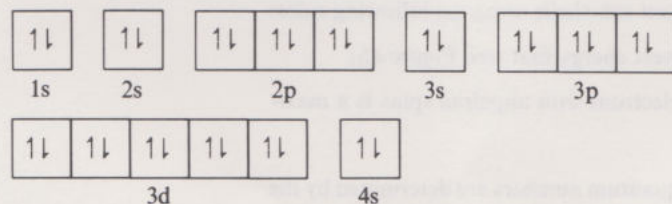
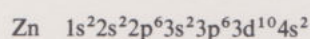
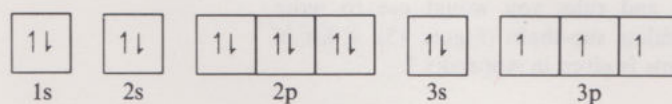
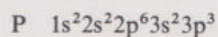


FIGURE 45 Order in which the sub-shells are filled.

Show the electronic structure of ground-state atoms of phosphorus (15), zinc (30) and cobalt (27), using both the s-p-d-f notation and the box method. (Atomic numbers are shown in brackets.) Use the sequence of sub-shells in Figure 45. Remember to fill the sub-shells of lowest energy first, irrespective of quantum number.

The structures are:



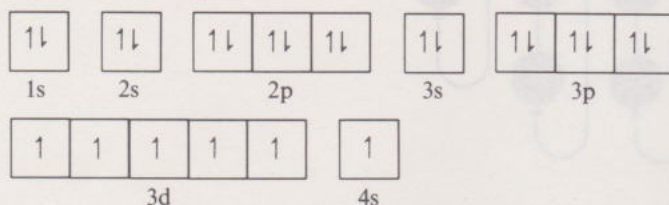
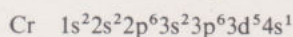
Now try chromium (atomic number 24).

No doubt you predicted the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$. If so, you have correctly interpreted the rules.

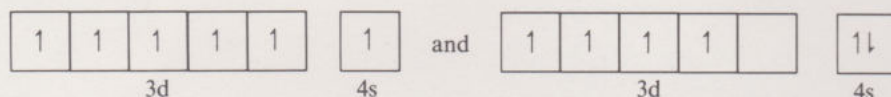
However, a few elements do not obey the rules precisely. In atoms with many electrons, as you can see from Figure 44, the energies of the outer sub-shells are sometimes very close together indeed, and occasionally the presence of electrons in, say, the 3d sub-shell changes the relative energy of the 4s sub-shell, so that sometimes it holds two electrons and sometimes only one. We know this from experiments.

Can you guess what type of experiment?

This sort of information is obtained from a detailed examination of the atomic spectra of elements. The analysis of such spectra is too complex for S101, but it shows the electronic configuration of chromium to be:



Clearly, from the anomalous electronic configuration of chromium, the energies of the configurations



must be very similar. *Knowing* the answer, it is possible to look for sensible reasons for it, but to predict it would be much more difficult.

You will remember that we have said that the results are obtained from a detailed examination of atomic spectra. Earlier in these Units you saw how an electron energy-level diagram could be obtained from a simple spectrum. Although this is much more difficult with a complex spectrum such as that of, say, cobalt, the general approach is the same.

9.2 Summary of Section 9

Here is a summary of the procedures and rules you would use to write electronic structures, given the order of filling sub-shells (Figure 45). A list of electronic configurations of all the elements is given in Appendix 2.

- 1 The atomic number of the element tells you the number of electrons.
- 2 These electrons are 'fed' into the electron sub-shells using the following rules:
 - (a) The electrons fill the sub-shells of lowest energy first (see Figure 45).
 - (b) Within any sub-shell, the number of electrons with unpaired spins is a maximum (Hund's rule).
- 3 The number of possible values of the quantum numbers are determined by the rules:

$$n = 1, 2, 3, \text{ etc.};$$

$$l = 0 \text{ to } n - 1;$$

$$m = -l \text{ to } +l$$

$$s = \frac{1}{2} \text{ or } -\frac{1}{2}$$

You probably no longer need apply rule 3 in this way; you probably just remember that:

an s sub-shell can contain two electrons (one pair, with opposite spins);

a p sub-shell can contain six electrons (three pairs);

a d sub-shell can contain ten electrons (five pairs);

within any atom, no two electrons can have the same set of four quantum numbers.

We can now summarize the information we have about the maximum number of electrons that can be contained in various sub-shells in the following way:

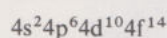
Electron shells with

principal quantum numbers $n =$	1	2	3	4
can contain	2	8	18	32 electrons

Electron sub-shells

denoted by values of $l =$	0	1	2	3
are represented by	s	p	d	f
and can contain	2	6	10	14 electrons

This means that a filled $n = 4$ electron shell consists of filled sub-shells represented by



Now that you have completed Section 9 you should be able to do the following things:

Show that you have some idea of what is meant by the terms 'Hund's rule', 'unpaired electrons'.

Represent the electronic configuration of atoms using the s-p-d-f notation or the 'box' notation, given the order of filling of sub-shells (Figure 45).

Try SAQs 34 and 35 to test your achievement of these Objectives.

SAQ 34 Write the electronic configuration of nitrogen using the box representation.

SAQ 35 Using the sequence of sub-shells given in Figure 45 write the electronic configuration of copper ($Z = 29$) in the s-p-d-f notation.

10 First ionization energies

We have said at various stages in these Units that our interest in the electronic structures of atoms arises mainly because electronic structure determines to a large extent the chemical properties of the elements. This dependence of chemistry on electronic structure is hardly surprising. As atoms approach each other to react it is the electrons that first interact or exchange; the diameter of an atom (the region containing the electrons) is about 10 000 times as large as the nuclear diameter.

Also, as you saw at the start of Section 6 (Figure 25), the energies needed to remove the first one or two electrons from an atom are much less than those needed to remove subsequent electrons. Not surprisingly, therefore, the energies required to remove the *first* electron from the atom of each element is for chemists an interesting quantity. One of the most valuable and chemically revealing sets of data that emerges from the study of electronic structure is the way that *first ionization energies*, I_1 , vary from element to element. Let us examine this variation.

first ionization energy, I_1

Table 6 lists the first ionization energies for the elements up to atomic number 20 (calcium).

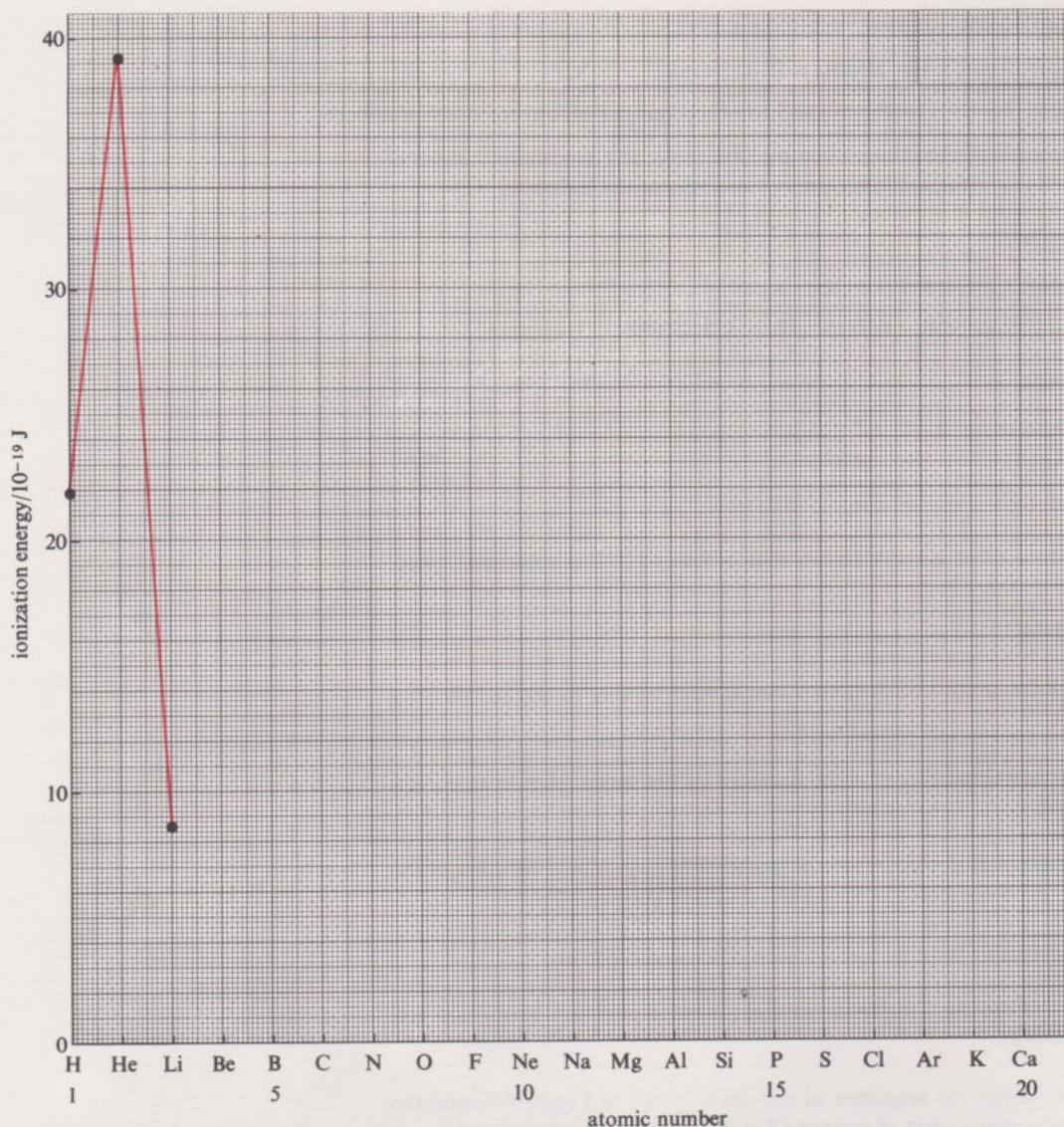


FIGURE 46 Your graph of ionization energy versus atomic number for the elements up to calcium.

Plot the first ionization energies against atomic number in Figure 46 (the first three points are given). List any features of the Figure that strike you.

In looking at the values in Table 6 or at the points on your plot, you are comparing the elements in order of increasing atomic number. From one element to the next an extra proton is added to the nucleus and an extra electron is added to the atom. The Table and plot compare the energy required to remove the *least* tightly bound electron from atoms of different elements. It seems likely that the last electron added in proceeding from one atom to another is the least tightly bound electron.

The most striking feature of your plot in Figure 46 is the way in which the ionization energies are arranged in ascending groups.

How many elements are there in each of the ascending groups which end at the three major peaks in the Figure?

These numbers are 2 (up to He), 8 (up to Ne) and 8 (up to Ar).

Is this reminiscent of any other data that you have encountered in the study of atomic structure in these Units?

If you compare the pattern of first ionization energies in Figure 46 with the ionization energies of individual electrons in the *same* atom, for example, argon in Figure 49 (p. 72), you will notice the same grouping of electrons 2, 8, 8. The reasons for these numbers should now be familiar from the discussion of quantum numbers and electron occupancy in Sections 5 to 9.

TABLE 6 The first ionization energies for the elements up to calcium

Atomic number	$\frac{I_1}{10^{-19} \text{ J}}$
1(H)	21.78
2(He)	39.22
3(Li)	8.63
4(Be)	14.93
5(B)	13.29
6(C)	18.03
7(N)	23.28
8(O)	21.81
9(F)	27.90
10(Ne)	34.54
11(Na)	8.23
12(Mg)	12.25
13(Al)	9.59
14(Si)	13.05
15(P)	16.80
16(S)	16.59
17(Cl)	20.84
18(Ar)	25.24
19(K)	6.95
20(Ca)	9.79

10.1 Ionization energies up to radon

We can, of course, extend our discussion of first ionization energies beyond calcium. Figure 47 shows a plot up to radon.

Do any of the features that you noticed up to atomic number 20 continue beyond there? List them.

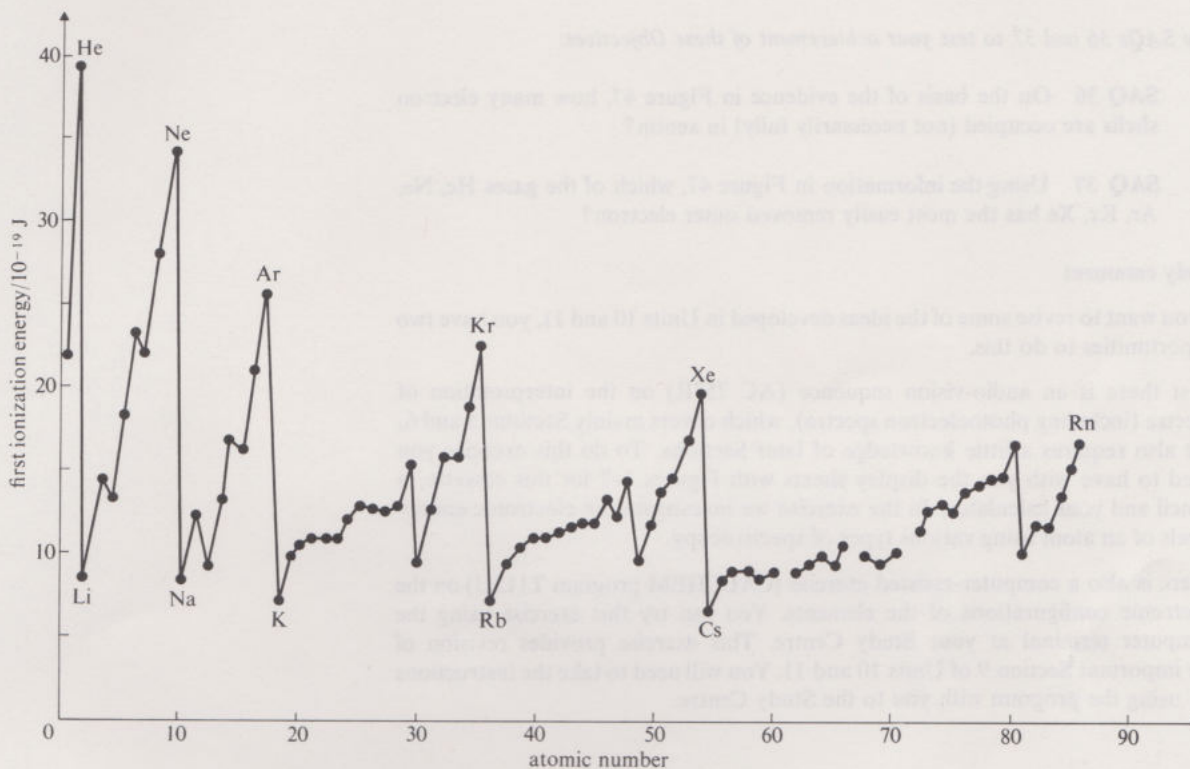


FIGURE 47 Graph of ionization energy versus atomic number for the first 86 elements.

The major peaks continue and each is immediately followed by a point in the minimum position. You probably also noticed similarities in the arrangements of the points leading up to each maximum.

You may also have noticed a similarity that underlies much of the emphasis we have placed on our study of electronic configuration. In Section 6 the elements we chose to study by photoelectron spectroscopy are precisely those that occur as single atoms: He, Ne, Ar, Kr and Xe. Notice their position at the peaks in the plot of first ionization energies (Figure 47). Their existence as single atoms (monatomic gases) results from their reluctance to combine chemically with other elements or themselves. This in turn suggests some connection between electronic configuration and chemical behaviour. Helium has a full sub-shell ($1s^2$). Each of the other atoms in this group has an outer shell with the configuration s^2p^6 (two full sub-shells), which appears to render these elements especially inert to reaction.

Unlike He, Ne, etc., the elements at the troughs of Figure 47 (Li, Na, K, Rb, Cs) are all particularly reactive. If this is related to their low ionization energies—their willingness to lose an electron—the connection between electronic configuration and chemical behaviour seems to strengthen.

These two examples of this connection illustrate the importance of an understanding of electronic configurations in the study of chemistry. However, before we close these Units, a word of caution. Do not be misled by these two groups of elements into believing that high ionization energy always equates with chemical inertness: fluorine, for example, with a relatively high first ionization energy, is nevertheless an extremely reactive element. Evidently, there are other factors that contribute towards chemical reactivity.

The intricate and fascinating relationship between electronic structure and chemical behaviour is a topic we shall examine more closely in Unit 13, after we have developed in the next Unit a feel for chemical substances and the way that they can behave in reactions.

Now that you have completed Section 10, you should be able to do the following things:

Show that you have some idea of what is meant by the term 'first ionization energy'.

Relate patterns in the first ionization energies of the elements to their electronic configurations.

Try SAQs 36 and 37 to test your achievement of these Objectives.

SAQ 36 On the basis of the evidence in Figure 47, how many electron shells are occupied (not necessarily fully) in xenon?

SAQ 37 Using the information in Figure 47, which of the gases He, Ne, Ar, Kr, Xe has the most easily removed outer electron?

Study comment

If you want to revise some of the ideas developed in Units 10 and 11, you have two opportunities to do this.

First there is an audio-vision sequence (AC 757R) on the interpretation of spectra (including photoelectron spectra), which covers mainly Sections 5 and 6, but also requires a little knowledge of later Sections. To do this exercise you need to have with you the display sheets with Figures 1-7 for this cassette, a pencil and your calculator. In the exercise we investigate the electronic energy levels of an atom using various types of spectroscopy.

There is also a computer-assisted exercise (CALCHEM program T112U) on the electronic configurations of the elements. You can try this exercise using the computer terminal at your Study Centre. This exercise provides revision of the important Section 9 of Units 10 and 11. You will need to take the instructions for using the program with you to the Study Centre.

APPENDIX 1 Relative atomic masses and atomic numbers of the elements

Element	Symbol	Atomic number	Relative atomic mass	Element	Symbol	Atomic number	Relative atomic mass
Actinium	Ac	89	227	Mercury	Hg	80	200.59
Aluminium	Al	13	26.981 53	Molybdenum	Mo	42	95.94
Americium	Am	95	243	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.17
Argon	Ar	18	39.948	Neptunium	Np	93	237.048 2
Arsenic	As	33	74.921 6	Nickel	Ni	28	58.71
Astatine	At	85	210	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.006 7
Berkelium	Bk	97	247	Nobelium	No	102	254
Beryllium	Be	4	9.012 2	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.999 4
Boron	B	5	10.81	Palladium	Pd	46	106.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.973 8
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	242
Californium	Cf	98	251	Polonium	Po	84	210
Carbon	C	6	12.011 15	Potassium	K	19	39.098 3
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907 7
Caesium	Cs	55	132.905 1	Promethium	Pm	61	147
Chlorine	Cl	17	35.453	Protactinium	Pa	91	231.035 9
Chromium	Cr	24	51.996	Radium	Ra	88	226.025 4
Cobalt	Co	27	58.933 2	Radon	Rn	86	222
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	247	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	254	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.955 92
Fermium	Fm	100	253	Selenium	Se	34	78.96
Fluorine	F	9	18.998 4	Silicon	Si	14	28.086
Francium	Fr	87	223	Silver	Ag	47	107.887 0
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.989 8
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulphur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	98.906 2
Helium	He	2	4.002 6	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.007 97	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038 1
Iodine	I	53	126.904 4	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.029
Lawrencium	Lr	103	257	Vanadium	V	23	50.942
Lead	Pb	82	207.2	Xenon	Xe	54	131.30
Lithium	Li	3	6.941	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.938 1	Zirconium	Zr	40	91.22
Mendelevium	Md	101	256				

APPENDIX 2 Electronic configurations of the elements

	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
1 H	1																	
2 He	2																	
3 Li	2	1																
4 Be	2	2																
5 B	2	2	1															
6 C	2	2	2															
7 N	2	2	3															
8 O	2	2	4															
9 F	2	2	5															
10 Ne	2	2	6															
11 Na	2	2	6	1														
12 Mg	2	2	6	2														
13 Al	2	2	6	2	1													
14 Si	2	2	6	2	2													
15 P	2	2	6	2	3													
16 S	2	2	6	2	4													
17 Cl	2	2	6	2	5													
18 Ar	2	2	6	2	6													
19 K	2	2	6	2	6		1											
20 Ca	2	2	6	2	6		2											
21 Sc	2	2	6	2	6	1	2											
22 Ti	2	2	6	2	6	2	2											
23 V	2	2	6	2	6	3	2											
24 Cr	2	2	6	2	6	5	1											
25 Mn	2	2	6	2	6	5	2											
26 Fe	2	2	6	2	6	6	2											
27 Co	2	2	6	2	6	7	2											
28 Ni	2	2	6	2	6	8	2											
29 Cu	2	2	6	2	6	10	1											
30 Zn	2	2	6	2	6	10	2											
31 Ga	2	2	6	2	6	10	2	1										
32 Ge	2	2	6	2	6	10	2	2										
33 As	2	2	6	2	6	10	2	3										
34 Se	2	2	6	2	6	10	2	4										
35 Br	2	2	6	2	6	10	2	5										
36 Kr	2	2	6	2	6	10	2	6										
37 Rb	2	2	6	2	6	10	2	6			1							
38 Sr	2	2	6	2	6	10	2	6			2							
39 Y	2	2	6	2	6	10	2	6	1		2							
40 Zr	2	2	6	2	6	10	2	6	2		2							
41 Nb	2	2	6	2	6	10	2	6	4		1							
42 Mo	2	2	6	2	6	10	2	6	5		1							
43 Tc	2	2	6	2	6	10	2	6	6		1							
44 Ru	2	2	6	2	6	10	2	6	7		1							
45 Rh	2	2	6	2	6	10	2	6	8		1							
46 Pd	2	2	6	2	6	10	2	6	10									
47 Ag	2	2	6	2	6	10	2	6	10		1							
48 Cd	2	2	6	2	6	10	2	6	10		2							
49 In	2	2	6	2	6	10	2	6	10		2	1						
50 Sn	2	2	6	2	6	10	2	6	10		2	2						
51 Sb	2	2	6	2	6	10	2	6	10		2	3						
52 Te	2	2	6	2	6	10	2	6	10		2	4						
53 I	2	2	6	2	6	10	2	6	10		2	5						
54 Xe	2	2	6	2	6	10	2	6	10		2	6						

	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
55 Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56 Ba	2	2	6	2	6	10	2	6	10		2	6			2			
57 La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58 Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59 Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60 Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61 Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62 Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63 Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65 Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66 Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67 Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68 Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69 Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70 Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			
71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85 At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6		2
98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2

Objectives for Units 10 and 11

Now that you have completed Units 10 and 11, you should be able to do the following things:

- 1 Define in your own words, recognize valid definitions of, and use in the correct context, the terms and concepts listed in Table A.
(All SAQs implicitly)
- 2 Represent elements, atoms, isotopes and ions using chemical symbols, given access to the information in Appendix 1.
(SAQs 1, 5 and 7)
- 3 Describe evidence (for example, experiments and results) for the existence of atoms.
(SAQ 2)
- 4 Describe and perform an experiment to determine roughly the size of an atom.
(SAQs 3 and 4)
- 5 Describe and interpret the results of an experiment in which atomic masses are measured.
(SAQ 6)
- 6 Estimate roughly the number of atoms in an object.
(SAQ 8)
- 7 Represent the numbers of protons, neutrons and electrons in an atom using symbols.
(SAQs 9, 11 and 12)
- 8 Describe the Rutherford model of the atom, giving roughly the dimensions of the atom and the nucleus, and describe how evidence for the model was obtained.
(SAQs 10 and 12)
- 9 Complete balanced equations depicting nuclear reactions.
(SAQs 14, 15 and 16)
- 10 Give examples of important nuclear reactions as outlined in Section 4 of Units 10 and 11.
- 11 Determine the age of a sample containing carbon, given its activity and Figure 13.
(SAQ 13)
- 12 Relate atomic spectra to energy changes on an electron energy-level diagram.
(SAQ 23)
- 13 Represent or interpret on an electron energy-level diagram the energy jumps corresponding to:
 - (a) emission spectra;
 - (b) absorption spectra;
 - (c) photoelectron spectra;
 - (d) ionization.
(SAQs 17, 18, 19, 21, 23, 29 and 30)
- 14 Appreciate that energy changes of electrons in atoms can only correspond to differences between 'allowed' energies.
(SAQs 20 and 33)
- 15 Outline a model of a light atom (one with atomic number, Z , less than 20) which is consistent with the information provided by its electronic and photoelectron spectra.
(SAQ 20)
- 16 Estimate roughly the ionization energy of an atom using the electron energy-level diagram derived from atomic spectra.
(SAQs 22 and 24)
- 17 Describe and identify experimental evidence for the existence of electron

shells, sub-shells, electron spin and degenerate energy levels.
(SAQs 26 and 31)

18 Relate the evidence in Objective 17 to the quantization of electron energy in the atom, and label the electron energy levels using quantum numbers.
(SAQs 25, 27, 28, 29, 30, 31 and 32)

19 Represent the electronic configuration of an element using the s-p-d-f notation or the 'box' notation, given the order of filling of sub-shells (Figure 45).
(SAQs 34 and 35)

20 Relate patterns in the first ionization energies of the elements to their electronic configurations.
(SAQs 36 and 37)

21 Describe and interpret the results of an experiment in which the electronic charge is measured. (Objective 21 is covered in TV 10.)

SAQ answers and comments

SAQ 1 (Objective 2) The symbol Ne can represent either the substance neon (a colourless gas which is present at a concentration of about 0.002 per cent in the atmosphere), or it can represent one atom of neon.

SAQ 2 (Objective 3) In Figure 1a the appearance of blurred dots indicates that the electron beam is scattered by small centres, which in this case are the individual atoms of thorium. Similarly, dots of light on the screen of the field-ion microscope (Figure 1b) indicate that the helium ions are formed at centres on the needle tip. These centres are atoms of tungsten.

SAQ 3 (Objective 4) We expect that from your results in Home Experiment 1 you should have calculated a value for the diameter of an atom of about 10^{-9} m. This gives a magnification of about 10^6 .

In our experiments we obtained an average area from one drop of about 30 cm^2 . The volume of one drop was very close to 0.01 cm^3 . Thus, the volume of stearic acid in one drop is

$$\begin{aligned} 0.01 \text{ cm}^3 \times 0.05 \div 100 \\ = 5 \times 10^{-6} \text{ cm}^3 \end{aligned}$$

Hence:

$$\begin{aligned} \text{thickness of film} &= \frac{\text{volume}}{\text{area}} \\ &= \frac{5 \times 10^{-6} \text{ cm}^3}{30 \text{ cm}^2} \\ &= 1.7 \times 10^{-7} \text{ cm} \end{aligned}$$

Now we told you to assume that this thickness is the diameter of one atom. Therefore, the diameter of an atom is approximately 10^{-7} cm or 10^{-9} m.

The distance between adjacent dots in Figure 1b is about 1 mm (10^{-3} m). The magnification in this Figure is therefore about $10^{-3}/10^{-9}$, that is, about 10^6 . In fact, as we warned you in the experiment, this estimate of the diameter is certainly high. A value of about 3×10^{-10} m is closer to the known diameter of an atom.

SAQ 4 (Objective 4) Approximately 10^{23} ; a hundred thousand million million million! The volume of a cup of tea is typically about 200 cm^3 . If each atom is assumed to be a cube of length l , then

$$\begin{aligned} \text{volume of atom} &= l^3 \\ &\approx 10^{-21} \text{ cm}^3 \text{ (approximately)} \end{aligned}$$

So

$$\begin{aligned} \text{number of atoms in cup of tea} &= \frac{\text{volume of tea}}{\text{volume of atom}} \\ &= \frac{2 \times 10^2 \text{ cm}^3}{10^{-21} \text{ cm}^3} \\ &\approx 10^{23} \text{ (approximately)} \end{aligned}$$

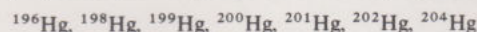
If the estimate of the atomic size is too small by about a factor of 3, the number of atoms should be about 10^2 larger than we have calculated—about 10^{25} atoms in a cup of tea. If you find it difficult to imagine a number as big as this, you are not alone. Atoms are indeed very small.

SAQ 5 (Objective 2) Hg^+ denotes a singly charged ion of mercury, that is, an atom of mercury which has lost one electron.

SAQ 6 (Objective 5) Mercury consists of isotopes (atoms having different masses). The seven peaks in the mass spectrum indicate that naturally occurring mercury has seven isotopes.

A mass spectrometer separates a mixture of atoms according to their mass. The appearance of several peaks in the mass spectrum shows that the sample, in this case mercury, consists of several types of mercury atom, which can be distinguished only by their mass. Atoms of an element having different masses are called isotopes.

SAQ 7 (Objective 2) The symbols for the isotopes present are:



Isotopes are denoted by the symbol for the element, accompanied by a superscript to show the mass number of the atom of that isotope. For example, the lightest isotope present appears to have a relative atomic mass very close to 196: hence its mass number is 196. The symbol for this isotope is therefore ^{196}Hg .

SAQ 8 (Objective 5) Chlorine must consist of a mixture of isotopes.

Atoms appear to consist of particles that have masses very close to one unit of relative atomic mass. Each isotope of an atom should therefore have a relative atomic mass which is very close to a whole number. If the relative atomic mass of an element is not close to a whole number, the element must consist of a mixture of isotopes. The relative atomic mass of an element is the weighted average of the relative atomic masses of the isotopes. Chlorine consists of two isotopes ^{35}Cl (75.5 per cent) and ^{37}Cl (24.5 per cent). The relative atomic mass of the element is then:

$$\begin{aligned} A_r &= (34.97 \times 0.755) + (36.96 \times 0.245) \\ &= 35.45 \end{aligned}$$

SAQ 9 (Objective 7) The symbols represent three different isotopes of hydrogen, each containing a different number of neutrons.

^1_1H represents an isotope containing no neutrons. It is usually just called hydrogen, or sometimes protium.

^2_1H represents an isotope containing one neutron. It is given a special name—deuterium.

^3_1H represents an isotope containing two neutrons. It is called tritium.

Remember that the subscript denotes the number of protons in the nucleus; one for a hydrogen atom. The superscript denotes the number of protons plus neutrons in the atom, that is, the mass number of the isotope.

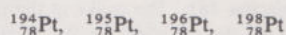
As you can see from the relative atomic mass of natural hydrogen (1.008), it predominantly consists of the isotope ^1_1H .

SAQ 10 (Objective 8) The surprising result of Rutherford's experiment, which revealed the presence of a small heavy nucleus with a positive charge, was the scattering of some α -particles by very large angles, occasionally back towards the source of α -particles. Only an electrical force acting at a very small distance would be large enough to account for this scattering. The electric charge in the atom is associated with a small body, which must be very massive in comparison to the α -particle; otherwise gold atoms would be knocked away from the foil by the α -particles. Knowing that atoms contain electrons (recall the photoelectric effect), which are very light and negatively charged, Rutherford proposed that the scattering was caused by a nucleus with a large mass (effectively the mass of the atom) and with a positive charge, which balances the negative charges on the electrons.

SAQ 11 (Objective 7)

Particle	Mass number	Charge
proton	1	+1
neutron	1	0
H atom	1	0
α -particle	4	+2
electron	0	-1

SAQ 12 (Objectives 7 and 8) Symbols for the isotopes are:



In his experiments, Chadwick was able to determine the charge on the nucleus and hence the number of protons in the nucleus (the atomic number). For platinum, this is 78 (written as a subscript). The relative atomic masses give the mass numbers of the isotopes and hence the numbers of protons plus neutrons in the atoms. The mass number is written as a superscript.

SAQ 13 (Objective 11) According to Figure 13, the wood is about 4750 years old. This dating process is based on the known rate of decay of ${}^{14}\text{C}$ and the assumption that the natural abundance of ${}^{14}\text{C}$ has not changed with time. Since the ancient Egyptians kept accurate calendars, the age of the pyramids is usually known precisely. The Sneferu pyramid is known to be about 4800 years old, in excellent agreement with the ${}^{14}\text{C}$ dating result.

SAQ 14 (Objective 9) The other product is ${}_0^1\text{n}$, the neutron. This experiment proved that the neutron existed as a particle and is generally recognized as the discovery of the neutron.

To conclude that the neutron is the other product, you have to balance the equation; the total mass (sum of the mass numbers) and the total charge (the sum of the atomic numbers) must be conserved. The mass number of the product is therefore $9 + 4 - 12 = 1$. Similarly, the charge of the product is $4 + 2 - 6 = 0$.

SAQ 15 (Objective 9) The atomic number of the product is 94. The addition of one neutron to the nucleus increases the mass number by one but does not change the atomic number. However, the resulting nucleus is unstable and it decays in two steps by emitting two electrons (${}_{-1}^0\text{e}$), which increases the atomic number of the nucleus by two. The product has atomic number 94 (see Appendix 1), so it is plutonium.

Plutonium is one of the man-made elements. The isotope produced in this reaction is ${}^{239}_{94}\text{Pu}$, which is itself unstable and in a reactor eventually undergoes fission to produce more neutrons and two other nuclei of lighter elements in much the same way as ${}^{235}_{92}\text{U}$ does (see Section 4.3). Plutonium could therefore power a nuclear reactor as ${}^{235}_{92}\text{U}$ does. Now the uranium isotope ${}^{238}_{92}\text{U}$ is relatively stable and much more abundant than ${}^{235}_{92}\text{U}$, but in a reactor with ${}^{235}_{92}\text{U}$, it gradually becomes converted to ${}^{239}_{94}\text{Pu}$, which can be used as fuel in another source of nuclear power, the 'breeder' reactor.

SAQ 16 (Objective 9) The atomic number is 98, so the product is californium.

Since both the charge and the total number of protons plus neutrons are conserved in nuclear reactions, the charge on the nucleus of the product is $92 + 6 = 98$; the nucleus contains 98 protons and is californium (see Appendix 1). Californium is another of the man-made elements, first obtained in 1950 by the American scientist Glen Seaborg at Berkeley, in California. The name of the element (and of elements 95 and 97) was chosen to honour the place where it was discovered.

SAQ 17 (Objective 13) The energy change corresponding to the red emission line is approximately $3.03 \times 10^{-19} \text{ J}$.

The red line in Spectrum B is close to $4.57 \times 10^{14} \text{ Hz}$ (or s^{-1}) in frequency.

The energy is given by:

$$E = hf$$

So, for the red line,

$$\begin{aligned} E &= 6.62 \times 10^{-34} \text{ Js} \times 4.57 \times 10^{14} \text{ s}^{-1} \\ &= 3.03 \times 10^{-19} \text{ J} \end{aligned}$$

Our reading of Spectrum B is only accurate enough to allow us to be sure of two significant figures in this answer.

SAQ 18 (Objective 13) $2.15 \times 10^{-19} \text{ J}$

The highest level has an energy of $5.18 \times 10^{-19} \text{ J}$ and the second lowest an energy of $3.03 \times 10^{-19} \text{ J}$. The difference is the energy of the photon that is emitted; $2.15 \times 10^{-19} \text{ J}$. (This is in the infrared region of the spectrum.)

SAQ 19 (Objective 13)

$$n = 1 \rightarrow 2 \text{ at } 2.47 \times 10^{15} \text{ Hz}$$

$$n = 1 \rightarrow 3 \text{ at } 2.92 \times 10^{15} \text{ Hz}$$

$$n = 1 \rightarrow 4 \text{ at } 3.08 \times 10^{15} \text{ Hz}$$

Adding $16.34 \times 10^{-19} \text{ J}$ to the energies of the red and blue photons listed in the last column of Table 4 gives the energies (relative to the lowest level, that is, $n = 1$) of the $n = 3$ and 4 levels. $16.34 \times 10^{-19} \text{ J}$ corresponds to the transition $n = 1 \rightarrow 2$.

$$(i) \quad 19.37 \times 10^{-19} \text{ J for the } n = 3 \text{ level}$$

$$(ii) \quad 20.43 \times 10^{-19} \text{ J for the } n = 4 \text{ level}$$

The frequency, f , of the photon absorbed when the electron is excited from the $n = 1$ level to each of these levels is obtained by dividing this energy, E , by h :

$$f = \frac{E}{h}$$

This gives the frequencies listed above.

SAQ 20 (Objective 14) (i) Yes (ii) Yes (iii) No (iv) No
In the ground-state atom, the electron is in the level $n = 1$.

(i) Only the first of the energies listed corresponds to a difference in energy between the $n = 1$ level and a higher energy level (see Figure 17).

(ii) Absorption of $22.74 \times 10^{-19} \text{ J}$ will excite the electron of the hydrogen atom from the $n = 1$ level into the continuum. The 'extra' $1 \times 10^{-19} \text{ J}$ above that required for ionization will be converted to kinetic energy of the emitted electron, so that an electron in the $n = 1$ level can be excited by a photon with energy $22.74 \times 10^{-19} \text{ J}$.

(iii) The atom cannot, however, absorb $17.5 \times 10^{-19} \text{ J}$, since this would give it an energy intermediate between that 'allowed' in the second and third quantum level.

(iv) Nor can it absorb $11.0 \times 10^{-19} \text{ J}$, which is not enough to bring it from the ground state to the first excited state. These last two photons will *not* be absorbed by a ground-state hydrogen atom.

SAQ 21 (Objective 13) (i) $21.34 \times 10^{-19} \text{ J}$, (ii) $8.55 \times 10^{-18} \text{ J}$, (iii) $1.92 \times 10^{-17} \text{ J}$

Reading from Figures 22 and 23, the frequency of the sixth line (in order of increasing frequency) is $1.29 \times 10^{16} \text{ Hz}$ for He^+ and $2.90 \times 10^{16} \text{ Hz}$ for Li^{2+} . These lines correspond to the jump between $n = 1$ and $n = 7$ in each case. The energy of the transition is obtained by multiplying the frequency f by h :

$$E = hf$$

For He^+

$$E = 6.626 \times 10^{-34} \text{ J s} \times 1.29 \times 10^{16} \text{ s}^{-1} \\ = 8.55 \times 10^{-18} \text{ J}$$

For Li^{2+}

$$E = 6.626 \times 10^{-34} \text{ J s} \times 2.90 \times 10^{16} \text{ s}^{-1} \\ = 1.92 \times 10^{-17} \text{ J}$$

For hydrogen, the energy of the $n = 1 \rightarrow n = 7$ transition is obtained by adding $16.34 \times 10^{-19} \text{ J}$ to the energy of the fifth line in Table 4 (Balmer series). This gives $21.34 \times 10^{-19} \text{ J}$. As the seventh level is getting close to the ionization energy, we can see how this energy increases as we go from H to He^+ to Li^{2+} .

SAQ 22 (Objective 16) The reason for the increase in ionization energy in the series H, He^+ , Li^{2+} is the increase in electrostatic attraction between the electron and the nucleus, whose positive charge increases as we go across the series. If the distance between the electron and nucleus were the same in all three cases, application of Coulomb's law would predict, for example, that the ionization energy of He^+ should be twice that of H because the charge on the He nucleus is +2 as against +1 for H. However, the electron is much closer to the nucleus in the case of He^+ than it is in H, which further increases the electrostatic attraction. It is actually about four times more difficult to ionize He^+ than H.

SAQ 23 (Objectives 12 and 13) Figure 48 shows the transitions:

- arrows 1 or 2;
- arrows 3, 4 or 5 (but see comment below);
- arrow 6;
- arrow 7.

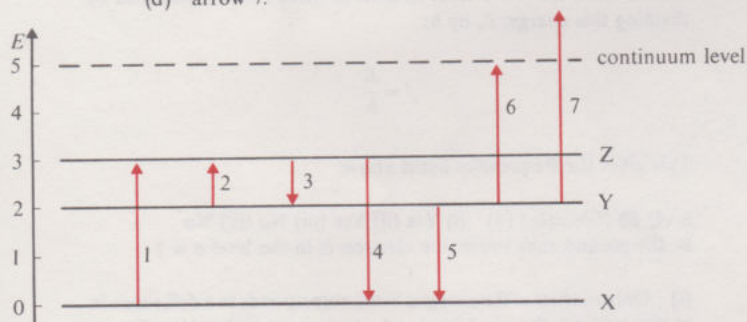


FIGURE 48 The transitions 1 to 7 for the hypothetical element pandemonium.

(a) An absorption occurs when an atom absorbs a photon and an electron is excited from a lower electron energy level to a higher electron energy level. In the ground state, only levels X and Y are occupied. The only higher level shown is Z. So the only absorptions possible are $X \rightarrow Z$ (arrow 1) and $Y \rightarrow Z$ (arrow 2). The transition $X \rightarrow Y$ cannot occur because in the ground state the level Y is already fully occupied.

(b) Emission occurs when an electron drops from a higher electron energy level to a lower electron energy level. It can only occur from excited states of the atom, in this case when at least one electron is in level Z. The resulting electron 'jump' will depend on the level that contains the vacancy (the ability to accept the electron now in level Z). If this is level Y, then emission 3 can occur. If it is level X, a transition from either level Z (arrow 4) or level Y (arrow 5) can occur.

(c) The first ionization energy is the energy required to excite an electron from level Y to the continuum level (arrow 6).

(d) A photoelectron results when an atom absorbs a photon and emits an electron. The photon with 4 energy units has insufficient

energy to ionize an electron in level X. Ionization from level Y can occur (arrow 7). The length of the arrow represents the photon's energy. So the energy of the photoelectron is $4 - 3 = 1$ energy unit.

SAQ 24 (Objective 16) The lowest ionization energy is 3 energy units.

The lowest ionization energy is the energy difference between the continuum level and the highest-occupied electron energy level in the ground-state atom (level Y):

$$I = 5 - 2 = 3 \text{ energy units}$$

SAQ 25 (Objective 18) The peaks in the photoelectron spectrum (A, B, C, D) are the sub-shells 1s, 2s, 2p and 3s, respectively. The number of electrons in each sub-shell are two in 1s, two in 2s, six in 2p and two in 3s. The electronic configuration is $1s^2 2s^2 2p^6 3s^2$.

From Figure 33 you know the order of filling sub-shells. The sequence 1s, 2s, 2p, 3s gives the labels for the first four sub-shells, and the relative ionization energies indicate that there are two sub-shells in the $n = 2$ shell, thus supporting this conclusion. An s sub-shell can hold up to two electrons and a p sub-shell can hold up to six. Since an atom of magnesium contains twelve electrons, each of the four sub-shells must be full. An important property of an atom with full sub-shells is that the distribution of electrons in the atom is spherically symmetrical, as indicated by Figure 12.

SAQ 26 (Objective 17) The production of photoelectrons with discrete energies (only five peaks) shows that the electrons in the atom have discrete energies. From the energy-distance relationship (Coulomb's law), we conclude that the electrons are contained in shells and sub-shells. The ionization energies of argon fall into three groups: A, B and C, D and E, indicating that there are three shells occupied by electrons in the argon atom. In the outermost two shells the presence of more than one peak in the photoelectron spectrum shows the existence of sub-shells.

SAQ 27 (Objective 18) An electron energy-level diagram for argon can be obtained simply by turning the photoelectron spectrum through 90° (Figure 49). Each peak in the spectrum corresponds to a sub-shell that contains at least one electron; the highest ionization energy corresponds to the innermost electrons.

In the electron energy-level diagram (as in the spectrum) the levels are arranged in groups. These groups are the electron shells, which are labelled with the principal quantum number, n . This quantum number has integral values from 1 upwards, as in Figure 49.

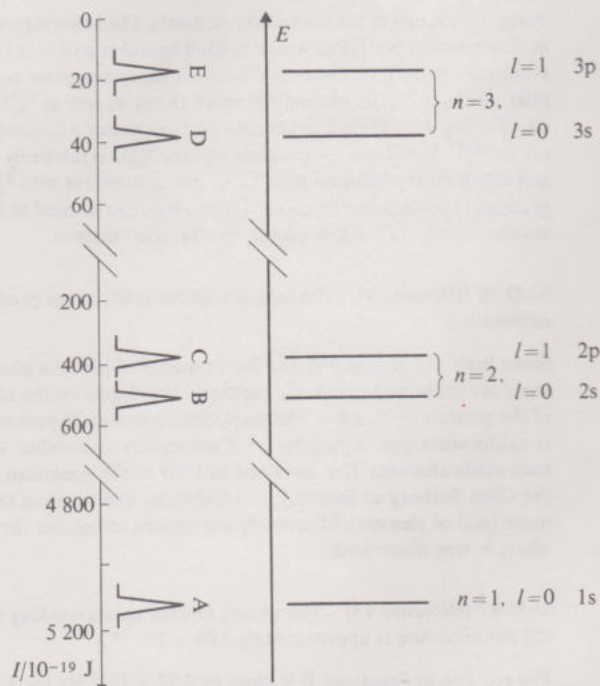


FIGURE 49 Labelled electron-energy level diagram for argon.

Within the shells, the existence of sub-shells is revealed by the closely spaced peaks within each group in the photoelectron spectrum. The sub-shells are labelled with a second quantum number, l . This can have values from zero to $(n - 1)$, so that within a shell there can be n sub-shells. Evidently, one sub-shell is unoccupied in the $n = 3$ shell. The values of l are shown in Figure 49. For historical reasons a letter is often used to label the sub-shells according to the value of l : s for $l = 0$; p for $l = 1$; d for $l = 2$. The levels in Figure 49 are therefore labelled 1s, 2s, 2p, 3s, 3p.

SAQ 28 (Objective 18) (i) and (iii), no effect; (ii) Na splits into two beams.

As you have learnt in Section 6.1, neon's ten electrons fill the 1s, 2s and 2p shells. All electron spins are paired, and there is no resultant magnetic effect. Also, in Figure 52 you will have deduced that all occupied levels in krypton are full, so there are no unpaired spins to interact with a magnetic field.

However, sodium has 11 electrons, so clearly at least one of these must be unpaired. In your energy-level exercise in Figure 33, only the electron in the 3s level is unpaired. Consequently, we would expect the Na beam to split into two beams in a non-uniform magnetic field, corresponding to (i) clockwise and (ii) anticlockwise spinning of the 3s electron.

SAQ 29 (Objectives 13 and 18) Application of a magnetic field causes the $n = 1$ level of atomic hydrogen to split into two levels, as we saw in Figure 42. For exactly the same reasons the $n = 2$ level should also split into two levels (Figure 50).

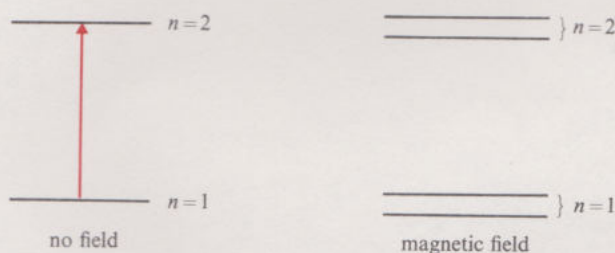


FIGURE 50 Splitting of hydrogen energy levels in a magnetic field.

There are now four electron energy levels between which we could imagine transitions might take place, so it is likely that more than one emission line will be observed. Although you could have no way of knowing this, only two of the possible four transitions are allowed, so the single line in the absence of a magnetic field splits into two when a strong magnetic field is applied.

SAQ 30 (Objectives 13 and 18) There should be no observed effect. Unlike hydrogen, helium has no unpaired electrons in the ground state ($1s^2$). If there is also no magnetic effect due to electron spin in the excited state ($1s^1 2s^1$) because the spins in the 1s and 2s levels are opposed, the presence of a magnetic field should have no effect on either state of the atom.

SAQ 31 (Objectives 17 and 18) All four electrons in the beryllium atom are paired; two in the 1s shell and two in the 2s sub-shell. There are no unpaired spins to produce any magnetic effect, and so this atomic beam is undeflected in an inhomogeneous magnetic field.

SAQ 32 (Objective 18) 7

In this case $2l + 1 = 7$.

SAQ 33 (Objective 14) 18

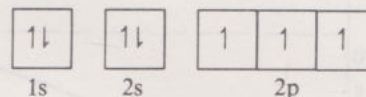
$n = 3$ shell will contain:

two electrons in the $l = 0$ (s sub-shell),

six electrons in the $l = 1$ (p sub-shell) in three degenerate orbitals with $m = +1, 0$, or -1 ,

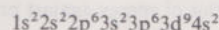
ten electrons in the $l = 2$ (d sub-shell) in five degenerate orbitals with $m = +2, +1, 0, -1$ or -2 .

SAQ 34 (Objective 19) The electronic configuration of nitrogen is represented by



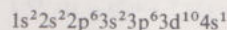
From the discussion of the four quantum numbers (Section 8.2), you can conclude that the arrangement of boxes representing orbitals is as shown above. Arrows representing the electrons (nitrogen has seven) are placed in the boxes, beginning with the lowest-energy orbital. Each box representing an orbital can accommodate a maximum of two electrons (see Section 7) of different spin: up \uparrow and down \downarrow . When a choice of boxes representing orbitals of the same energy (degenerate levels) is available, as for 2p, Hund's rule states that there should be a maximum number of unpaired electrons. Hence, for nitrogen the three 2p electrons each occupy different orbitals as shown above.

SAQ 35 (Objective 19) If you wrote for the electronic configuration of copper:



then you applied the rules outlined in Section 9 correctly. Copper has an atomic number of 29 and the atom contains 29 electrons. These electrons are placed in boxes which represent orbitals. The boxes are arranged in order of energy.

However, you saw in Section 9 that as the number of levels increases their energies get closer. For chromium, the 3d and 4s levels are so close that both levels are only partially occupied. The same is true for copper. Its electronic configuration is:



Copper and chromium are the only exceptions to the general rule that the 4s sub-shell fills before the 3d sub-shell.

SAQ 36 (Objective 20) The sharp maximum at helium corresponds to a full 1s shell. The very sharp maxima that occur for the gaseous elements Ne, Ar and Kr all correspond to the seemingly stable arrangement of outermost electrons $s^2 p^6$, in which the s and p sub-shells are full. It seems likely that xenon continues this trend. If so, xenon has the outer electronic configuration $5s^2 5p^6$. Therefore, we conclude that five electron shells are occupied in xenon.

SAQ 37 (Objective 20) Xenon has the most easily removed outer electron. As you will discover in Units 12 and 13, when some elements react, they often do so by their atoms gaining, losing or sharing electrons. Xenon, in fact does react to form compounds, whereas helium, neon and argon are not known to form compounds.

Answers to questions in the text

Answer to question on p. 30

The bluish-white street lights are mercury lamps. Compare their spectrum with your sketch of the spectrum of your own mercury lamp or with Spectrum C on the colour plate.

Answer to question on p. 37.

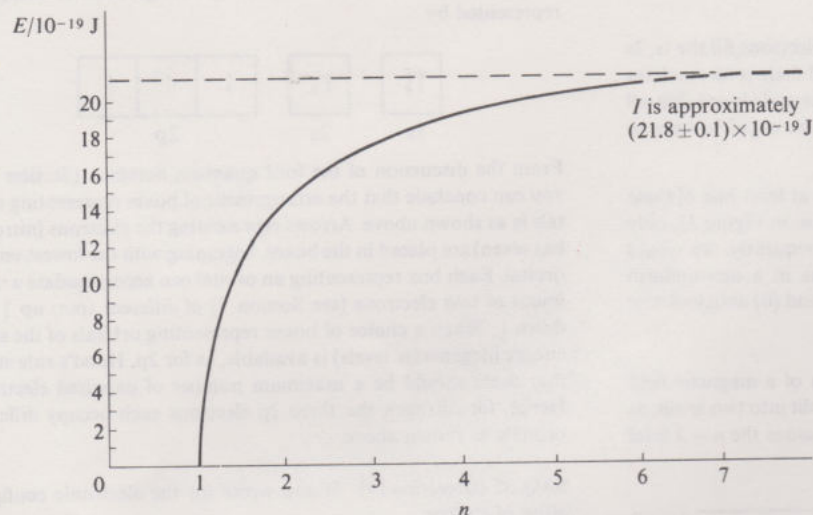


FIGURE 51 Plot of energy against principal quantum number, n .

Answer to question on p. 40

Estimate of ionization energy of hydrogen from Figure 19:

$$f = (3.27 \pm 0.03) \times 10^{15} \text{ Hz}$$

$$E = hf$$

$$= 6.626 \times 10^{-34} \text{ J s} \times 3.27 \times 10^{15} \text{ Hz}$$

$$= (21.7 \pm 0.2) \times 10^{-19} \text{ J}$$

Answer to question on p. 47

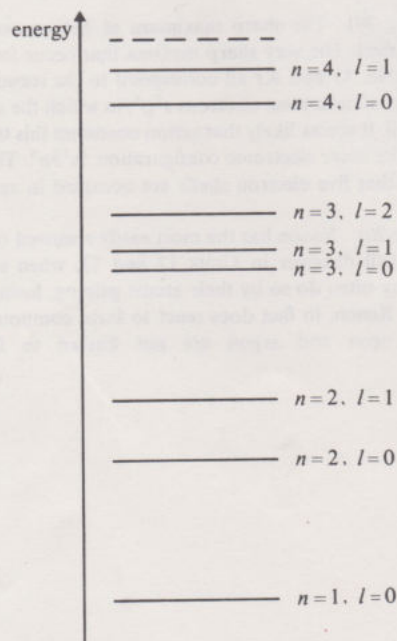


FIGURE 52 Electron energy-level diagram for krypton.

Answer to question on p. 49

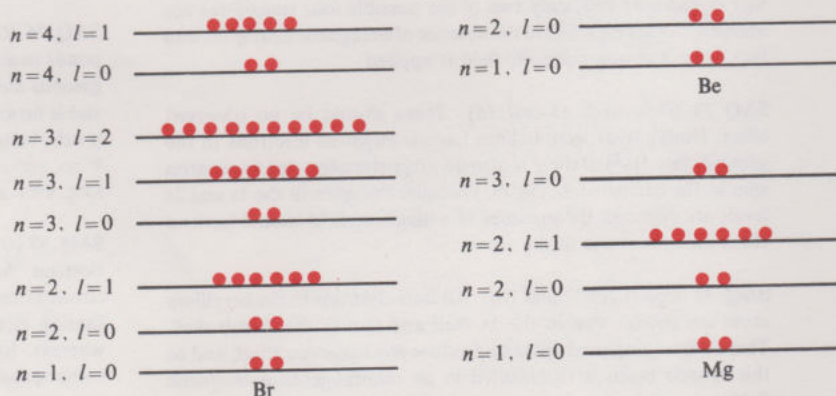


FIGURE 53 Answers to exercise on energy levels.

Acknowledgements

Grateful acknowledgement is made to the following sources for material used in these Units:

Figure 1a from A. V. Crewe *et al.* (1970) Visibility of single atoms, in *Science*, 168 copyright © 1970 the American Association for the Advancement of Science;
Figure 1b by courtesy of Dr R. G. Forbes, the University of Aston in Birmingham.

S101 Science: A Foundation Course

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